The Dissertation Committee for Ambarish Banerjee Certifies that this is the approved version of the following dissertation:

Breaking and Curing Rates in Asphalt Emulsions

Committee:

Jorge A. Prozzi, Supervisor

Amit Bhasin

Brian Korgel

Kevin J. Folliard

Zhanmin Zhang

Breaking and Curing Rates in Asphalt Emulsions

by

Ambarish Banerjee, B. Tech, M.S.E.

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Dedication

I would like to dedicate this work to my family: my father, my mother and my brother; who have always supported my choices and have always been with me during my good and bad times.

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I would like to thank my advisor, Dr. Jorge A. Prozzi, for help and guidance that he lent to me, without whom this work could never been completed.

Breaking and Curing Rates in Asphalt Emulsions

Ambarish Banerjee, PhD

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Supervisor: Jorge A. Prozzi

This PhD dissertation addresses a number of issues pertaining to the use and application of surface treatments using asphalt emulsions. The work conducted as part of this research study shows in detail the problems associated with the state-of-practice and how these issues can be addressed using a scientific and rational approach as opposed to the experience-based approach which is prevailing currently. The first objective of this research study focuses on developing a methodology to determine the total amount of evaporative water loss of an emulsion before the aggregates are placed. An algorithm is presented that can be used by field inspectors and practitioners for the optimal timing of chip placement. The second objective focuses on another key aspect associated with the constructability of surface treatments, i.e., the optimal time to open a new surface treatment to traffic. Laboratory tests were conducted on the emulsion and aggregates to measure the rate of moisture loss and the evolution of the rheological properties as function of time. This was related to the field measured evaporation rates to determine the minimum stiffness required for optimal performance of the chip seal towards adequate resistance to raveling. The final objective of this dissertation focuses on developing a theoretical understanding of the current flowing through a circuit when an

emulsion separates into its constituent phases when placed in an electric field. The measured current depends on a set of material properties that include the emulsion's viscosity, surface potential, and dielectric of the medium and the strength of the electric field. A theoretical formulation was developed that relates the current flowing through the circuit with the mobility of the charged particles and the bulk charge density. The proposed theory was further utilized in developing a test procedure to quantify the breaking characteristics of asphalt emulsions. Results demonstrated that the parameters obtained from these tests were repeatable and different for different types of asphalt emulsions. It was also noticed that for a given type of emulsion the test method is sensitive to factors such as water content and partial breaking due to mechanical agitation.

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Chapter 1: Introduction

1.1. INTRODUCTION

Asphalt products for road construction include asphalt cements, cutback asphalts and emulsified asphalts. Typically, the asphalt binder has a high viscosity under ambient conditions which requires heating the material in order to reduce its viscosity and improve workability. The purpose of producing emulsified or cutback asphalt is to reduce the temperature at which it can be applied. From an environmental point-of-view, reduced temperatures and the reduction of volatile components such as aliphatic hydrocarbons are beneficial considering their health hazards for the work crew. Emulsified asphalt products are particularly advantageous in this sense as cutback asphalts involve dissolution of asphalt binder in solvents like diesel, kerosene or benzene which require evaporation of the volatile solvents which can pose fire hazards. Furthermore, high crude prices combined with budgetary constraints on highway agencies makes cutback asphalt a relatively inferior choice economically.

Emulsions are defined as suspensions of two immiscible substances that are stabilized using a surface active agent (e.g. soap). An asphalt emulsion is composed of three ingredients – asphalt cement, water, and an emulsifying agent. It is a heterogeneous system with two or more liquid phases consisting of a continuous liquid phase and at least a second liquid phase, dispersed in the first phase in the form of fine droplets (EN ISO 862, 1984). This implies that an emulsion is an imposed mixed state which qualifies as thermodynamically unstable or metastable. Natural forces tend to separate these two phases which will eventually form a stable state but on a time scale this process might

last from a few seconds to several months (SFERB, 2008). Therefore in order to reduce the chances of a spontaneous separation of the two phases, surface active agents (a.k.a. surfactants/soaps/emulsifiers) are introduced to reduce the surface tension of the droplets of the dispersed phase and to stabilize the two phases.

In the absence of these external forces, emulsions tend to separate into its constituent phases to achieve a thermodynamically stable state. However, most emulsions have a relatively long shelf life. Interestingly, asphalt emulsions are designed to break within a desired period of time and this duration depends on the application. Emulsions commonly used for surface treatment applications are expected to have a shorter shelf life as opposed to those used for cold mix applications. However, premature breaking (separation of the constituent phases) of the asphalt emulsion is not desired as it can render a particular emulsion unsuitable for its intended use.

It is important to introduce two definitions in this context: (i) breaking, and (ii) curing of asphalt emulsions. Breaking is defined as the combined sedimentation and coalescence of emulsified drops of the dispersed phase so that they will settle out of the carrier liquid; can be accomplished mechanically with or without the aid of chemical additives to increase the surface tension of the droplets (McGraw Hill, 2003). Curing of an emulsion, on the other hand, refers to the combination of phenomena which result in the removal of the water from the bituminous material, after the breaking phase is completed or is at least sufficiently initiated (SFERB, 2008). The combination of these two processes improves the mechanical properties of the product prepared with the

emulsion. The combination of these two processes helps the binder achieve the desired strength properties.

It is important to realize that there are different formulations of asphalt emulsions to address specific construction needs. The nomenclature of asphalt emulsions have been also designed to address this specific requirement. Primarily, asphalt emulsions are classified as rapid-setting (RS), medium-setting (MS) and slow setting emulsions (SS). Furthermore, a prefix “C” is added to denote if the particular formulation is a cationic (the asphalt droplets are positively charged) emulsion. In addition, the number “1” or “2” is used as a suffix to denote the viscosity of the emulsion where “1” denotes the particular emulsion having viscosities below 150 SFS (Saybolt Furol Seconds) at 77°F (25°C).

The use of polymers to produce modified asphalt binders has created a whole new family of asphalt emulsions types. Letters P (Polymer-modified) or L (Latex-modified) is suffixed to the name of base emulsion to designate emulsions that utilize polymer modified binders. Certain highway agencies use an additional cationic sand-mixing grade (CMS-2S) that contains more solvent than usual (Asphalt Institute, 2008). Therefore, according to the nomenclature described above, a cationic rapid setting emulsion with high viscosity will be abbreviated as “CRS-2” and the same when modified with polymers will be referred to as “CRS-2P”.

Given that the classification of asphalt emulsions involves the determination of their breaking properties, it is important to have well-defined test procedures that will aid their quantification. Currently, there are two commonly used for this purpose: (i) Demulsibility and cement-mixing test, and (ii) Sand mixing test. Demulsibility and

cement mixing tests are performed on the emulsion to determine the time it takes for the emulsion to break and cure. The demulsibility test is recommended for rapid setting emulsions whereas the cement mixing test is recommended for slow setting emulsions (TxDOT, 2002). In these tests, a solution of water and sodium chloride or cement is used to break the emulsion. The (broken) emulsion is then sieved to determine the amount of asphalt that has coagulated. Another example of a test to measure breaking rate involves adding sand and fillers to the emulsion at a certain rate and then using a colorimetric method to determine a breaking index for the emulsion (ASTM D7496, 2009).

However, a major drawback of these tests is that they do not provide any information with regards to the material's fundamental properties. Furthermore, it has also been pointed out that the test results might be subjective as interpretation of colors can vary from person to person. Given these shortcomings, it is therefore necessary to develop test procedures that rely on fundamental material properties and provide quantitative definitions regarding the material's breaking characteristics.

1.2. USE OF ASPHALT EMULSIONS

Asphalt emulsions find their greatest use as paving material, more specifically for surface treatment applications. The term surface treatment refers to single, double or triple application of an asphaltic material, each covered with aggregate and constructed over an existing pavement (chip seals) or prepared base course (seal coats).

The construction of chip seals involves spraying a thin layer of asphalt emulsion (~2mm) and letting it partially cure. At this time, a chip-spreader places a layer of aggregates on the road surface. It is important that the aggregates are neither placed too

early nor too late. Improper timing of aggregate placement can lead to premature failures of the surface treatment due to tire pickup or result in inadequate bonding with the asphalt emulsion. The next step involves compaction, which is mostly done using pneumatic rollers as steel rollers pose the problem of bridging over uneven surfaces. During this operation, the road is temporarily closed until the newly constructed surface treatment develops enough shear strength to withstand the shear stresses generated by moving traffic.

Surface treatment practitioners encounter a number of construction related problems involving emulsified and cutback asphalt binders. One of the major constructability issues faced in the field is loss of aggregate. Loss of aggregates may be triggered by a number of issues including improper timing of placement of emulsified asphalt or cover aggregates, insufficient binder to cement the cover aggregates to the existing surface, and opening to traffic moving at the posted speed limit before proper adhesion has developed.

The state of practice as of today is mostly based on experience. There is little published literature that provides guidelines on the optimal time to place the aggregates or to open to traffic. One of the primary focus areas of this research work involves establishing a formalized procedure for making these key decisions based on laboratory test results on curing and breaking rates of asphalt emulsions that are cross-validated against field performance data. The first two objectives of this study will aim at addressing the issues pertaining to state-of-practice for construction of surface treatments

based on laboratory test results that have good correlation with field performance in actual projects.

Asphalt emulsions are also widely used for other preventive maintenance applications including fog seals, prime coats and tack coats. A key concern for field engineers and inspectors arises from the fact that they are unable to determine if the emulsion meets the desired requirements which includes its breaking characteristics, dilution ratio (ratio of asphalt cement to water in the emulsion) or in rare cases, if the material itself has prematurely broken before its application. In rare occasions, it has also happened that the wrong emulsion has been delivered to the project site. A quick yet robust test for determination of the dilution rates can potentially address these problems. The third and final objective of this study addresses this specific research need. The author proposed a new test procedure that uses electrokinetic principles for characterizing the breaking characteristics of an emulsion. The suggested methodology is capable of distinguishing between different emulsions or changes within a given type of emulsion compared to a reference sample (Banerjee et al., 2012). The proposed test method applies an electric potential across an emulsion sample that serves as an electrolytic medium. The current flowing through this setup destabilizes the emulsion and causes the asphalt droplets to break and deposit on one of the electrodes. The concomitant parameters (from the relationship between current and time) were found to be sensitive to the inherent properties of the emulsion, such as, its dielectric constant, zeta potential and viscosity. Furthermore, the proposed methodology was also successful in differentiating between

formulations of the same emulsions at different dilution rates with respect to the reference sample.

1.3. BACKGROUND

The removal of water from an emulsion is a two-step process which includes destabilization of the electrostatic forces in the emulsion and subsequent removal of water through evaporation. The former is more commonly known as ***breaking*** of the emulsion while the later is referred to as ***curing*** of the emulsion.

Emulsion breaking signifies the phenomena in which the majority of the droplets of the emulsion undergo an irreversible process that results in the formation of a continuous macroscopic asphalt binder phase (SFERB, 2008). The emulsions are formulated to have a sufficient level of potential repulsion between the adjacent particles to prevent premature coagulation. The particles coalesce only if modification occurs, at least locally within the surfactant films (SFERB, 2008). This can be due to a variety of reasons including:

- A change in the hydrophilic and lipophilic balance of the emulsifier
- A change in acidity (pH)
- An increase in the ionic force of the medium
- Adsorption of the surfactant by the mineral aggregates

1.3.1. Breaking and Curing of Emulsions

Breaking and curing of emulsion is a physico-chemical process. It is governed by the energy differences among the forces acting between the dispersed particles which include

van der Waals interactions, electrostatic forces and stearic repulsion. The DLVO (Derjaguin and Landau, Verwey and Overbeek) theory suggests that the stability of a colloidal system is determined by the sum of these van der Waals attractive (V_A) and electrical double layer repulsive (V_R) forces that exist between particles as they approach each other due to the Brownian motion they are undergoing (Derjaguin et al., 1941). This theory proposes that an energy barrier resulting from the repulsive force prevents two particles approaching one another from adhering together. Figure 1.1 illustrates the forces acting between two particles as a function of separation distance. The figure indicates that at very low separation distances, the force acting between two adjacent particles is negative implying that there is a strong attraction between the particles to coalesce together. However, as the separation distance increases, it results in the emergence of the primary maximum which indicates that there is strong repulsive force acting between the dispersed particles. If the particles collide with sufficient energy to overcome that barrier, the attractive force will pull them into contact and they will adhere strongly and irreversibly together. Therefore, if the particles have a sufficiently high repulsion, the dispersion will resist flocculation and the colloidal system will be stable. However, if a repulsion mechanism does not exist, flocculation or coagulation will eventually take place.

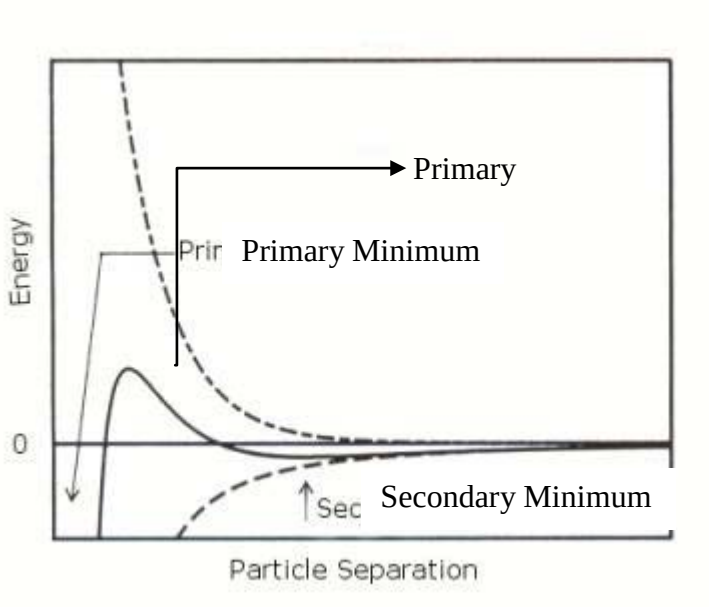


Figure 1.1: Schematic showing particle free energy as function of separation distance

Figure 1.1 also demonstrates that there is a possibility of a secondary minimum to co-exist. This might result in the formation of weaker flocs and therefore they can be reversed through some sort of mechanical disturbance or agitation. The electrostatic forces, due to the presence of the double diffused layer, bridge the dispersed and continuous phases in the emulsion. The counter ions present in the continuous phase associate with the ions in the double diffused layer, thus further contributing to the stability of the emulsion. Given an energy source that is strong enough to overcome these electrostatic forces, the repulsive force that stabilizes the emulsion will be overcome resulting in the separation of the continuous phase (water) from the dispersed phase (asphalt). This external source can be the solar radiation or other means like mechanical rolling (compaction) which can also lead to breaking and curing of the emulsion (Hanz et al., 2009). Water evaporation can occur fairly fast under favorable weather conditions,

but high humidity, low temperatures, or rainfall will retard the curing process (Asphalt Institute, 2008).

It is noteworthy that the curing of an emulsion is not only an evaporative process but also diffusion controlled and therefore its kinetics are governed by the rate of diffusion of water through the coalescing binder (Holleran and Motina, 2006). The end result of the curing phase is a continuous cohesive film that holds the aggregate in place with a strong adhesive bond.

Thus, curing refers to the combination of processes which result in the removal of the water from the bituminous material, after the breaking phase is completed or is at least sufficiently initiated. This improves the mechanical properties of the product prepared with the emulsion (SFERB, 2008). The statement above implies that the development of stiffness as well as its ability to hold the aggregates back will be governed by the rate of moisture removal from the system. Early placement of aggregates can lead to tire pickup by rollers, while delayed placement of stones will require more compaction effort or in some cases improper embedment of stones which are dislodged within the first few weeks of opening to traffic (King, 2010).

1.3.2. Premature Failures in Chip Seals due to Improper Construction Practices

As highlighted earlier, asphalt emulsions find their greatest use as a construction material for surface treatment applications. One of the most prominent challenges that are often encountered with the use of asphalt emulsions involves early loss of cover aggregates, also known as raveling. Loss of aggregates may be due to inadequate development of the adhesive bond between the emulsified binder and the cover aggregate. When a newly

constructed chip seal is opened to traffic too early, the improperly bonded aggregates (due to inadequate curing) may be dislodged by the moving loads. Thus it is necessary to estimate the setting rate of the emulsion as it breaks and hardens and optimize the time to open the road to traffic at highway speeds. Knowing the rate of curing (and breaking) of the emulsion is also important to predict the rate at which it gains strength.

Epps et al. (2001) reported that loss of aggregates at high and low temperatures were the primary failure mechanisms of chip seals and were controlled, at least in part, by the binder properties. At high temperatures they hypothesized that loss of aggregates was triggered by the high shear stresses generated on the road surface under the action of wheel loads. When these shear stresses exceed the shear strength of the asphalt binder, the wheel loads dislodge the aggregates from the road surface.

The Strategic Highway Research Program (SHRP) found that the performance of asphalt binders at high temperature is governed by the complex shear modulus (G*) and the phase angle (δ). The complex shear modulus is defined as the ratio of the shear stress amplitude to the shear strain amplitude. The phase angle refers to the time lag between the maximum applied shear stress and the maximum resulting shear strain. The study recommended using the term G*/sin δ as the high temperature parameter. The underlying assumption was that a higher G*/sin δ is accompanied by lower energy dissipation in a load cycle which translates into improved resistance to permanent shear deformation (Roberts et al., 1996). In the context of surface treatment binders, higher values of G*/sin δ would reflect in higher resistance to shear deformation under the action of traffic loads. Recent studies have pointed out that the thin film of asphalt residue left behind

from a fully cured emulsion is subjected to high levels of shear strains as soon as the surface treatment is opened to traffic (Redelius, 2006). Thus it is essential that the binder has developed adequate strain resistance to prevent aggregate loss due to moving wheel loads. Testing the emulsion residue in a dynamic shear rheometer (DSR) can simulate this particular form of distress provided that the test is conducted at high strain levels (Hanz et al., 2009).

1.3.3. QC/QA of Emulsified Asphalt and its Role in Chip Seal Construction

In addition to the problems highlighted above, the following common concerns pertaining to the use of asphalt emulsions were also identified in a recent survey of field inspectors and engineers from the Texas Department of Transportation (Prozzi et al., 2011):

- Uncertainties associated with the rate at which an emulsion breaks and cures when used at a construction job site.
- Premature breaking of the emulsion during transport or within the distributor trucks resulting in a complete shutdown of the job or choking of the nozzles in the spreader bars.
- Higher than expected viscosity of the asphalt emulsion that is delivered to the job sites, which results in undesirable wetting properties of the emulsion.

The reason behind reservations regarding the use of asphalt emulsions is due to the subjectivity associated with the results obtained from testing procedures that are currently available. Furthermore, some of these tests are only suitable for a laboratory environment as they require delicate instrumentation. For example, demulsibility and cement mixing tests are performed on the emulsion to determine the time it takes for the

emulsion to break and cure. However, these tests are typically not used in the field due to the difficulty in breaking and sieving the materials. Another limitation of these tests is that in some cases the results can be subjective.

The viscosity of asphalt emulsions and presence of oversize particles (e.g. due to partial breaking) are measured to ensure that the emulsion is suitable for construction. The Saybolt Furol Viscosity test is used by several state agencies to determine the viscosity of the asphalt emulsion (ASTM D7496, 2009). The extensive instrumentation needed to perform this test limits its use to a laboratory environment. A recent study evaluated the use of Shell cups as a rapid field test to determine the viscosity of the emulsion (Prozzi et al., 2010). The study demonstrated that the viscosity of emulsions measured using shell cups was repeatable and accurate. However, qualifying the use of an emulsion solely on the basis of its viscosity can be misleading as viscosity does not necessarily reflect the stability or condition of the emulsion.

In summary, the state of the practice is mostly based on tests that can either be performed only in a laboratory environment or are simple but yield qualitative results that need experience to interpret. This highlights the need for robust test methods that can be employed in the laboratory or in the field to characterize the emulsion and assess its suitability for construction (e.g. to assess whether or not the emulsion is partially broken when delivered to the construction site).

Thus the literature review shows two primary areas of concern related to the use of asphalt emulsions were identified. The first is associated with the state of practice for construction of chip seals including loss of aggregates that might happen during

compaction (rolling) or at later stages after the newly constructed chip seal is opened to traffic moving at the posted highway speed. The second aspect is associated with the overall quality of the emulsion that is delivered to the construction site. Premature breaking during transport, higher than expected viscosity of the plant emulsion and over-dilution of the plant emulsion are the areas of major concern for the latter.

1.4. OBJECTIVE

Figure 1.2 summarizes the work that has been carried out as part of this research study. As it can be seen, the overall framework of this dissertation broadly addresses day to day issues that are faced in the chip seal construction industry. It is understood that addressing the highlighted issues will help the construction industry replace the current experience-based approach with a more rational and scientific approach.

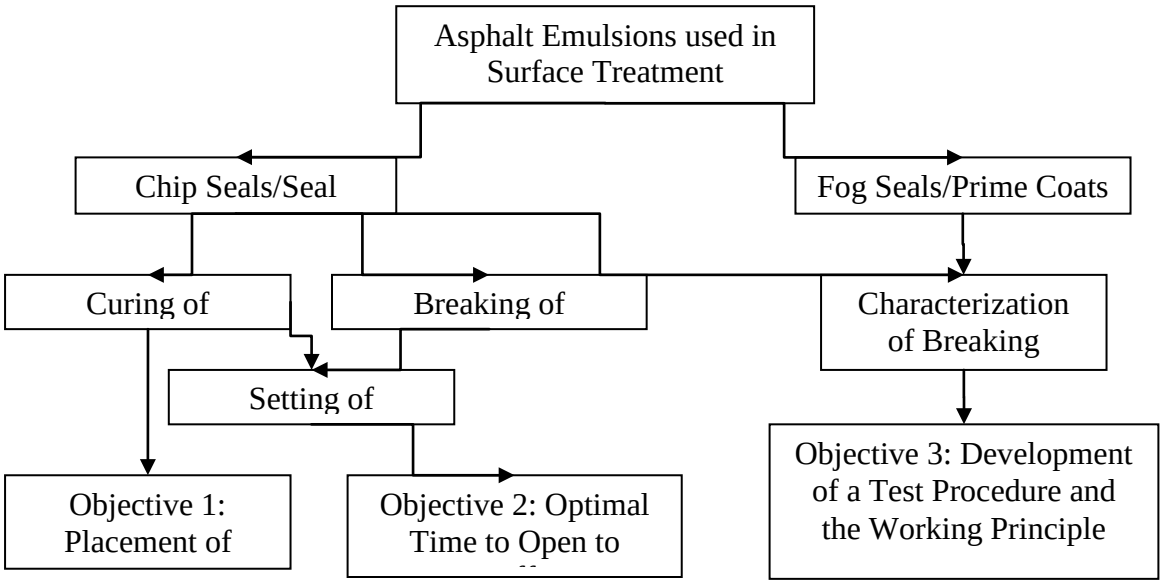


Figure 1.2: Scope of this Work

One of the major constructability issues related to the use of emulsions in the field is the loss of aggregates and the consequent economic losses, safety impacts and environmental effects. Loss of aggregates may be triggered by a number of factors such as improper timing of placement of emulsified asphalt or cover aggregates, insufficient binder to hold the cover aggregates to the existing surface, and allowing fast traffic before proper adhesion is developed. Thus, the underlying reason for loss of aggregates is the inadequate development of the adhesive bond between the emulsified binder and the cover aggregate. If the aggregates are placed too late, the emulsion's viscosity would have increased due to partial setting resulting in improper or inadequate coating of the aggregate. Therefore, it is necessary to estimate the rate of moisture lost due to evaporation as it will govern the evolution of the mechanical properties of the binder and determine the optimal timing for placement of the aggregate after spraying the emulsion. In this context, one of the primary objectives of this study is the development of a predictive model to quantify the amount of water lost as a function of time and changing weather conditions.

Secondly, the foregoing discussion illustrated that optimal timing of opening a newly constructed chip seal to traffic is key to having superior performance. Otherwise, early loss of aggregates can become a major problem, often leading to premature failures in chip seal applications. Most early failures in chip seals are due to premature opening of the road to normal traffic. A rule of thumb that is popular in the chip seal industry is that traffic should be restricted to a maximum speed of 25 mph until the emulsion sets,

compaction has been completed and the first brooming is done. The restriction in the posted speed limit is imposed by employing a pilot vehicle following construction.

Thus, the next objective of this study is to determine the optimal time to open a newly constructed chip seal to normal traffic without restricting the posted speed of the traffic, based on a scientific approach that captures the several dimensions understood to be instrumental in determining the setting characteristics of the emulsion in the field. During this part of the study, a model was developed that can predict the setting trends of the emulsion as a function of time, changing weather conditions, nature of emulsion and type of aggregates. It has been also pointed out in past research that the stiffness of the binder plays a key role in determining the resistance to raveling under shearing action of traffic loads. As mentioned earlier, the loss of moisture due to evaporation helps the material to set and gain adequate resistance to shear strain as its gaining stiffness. Therefore the predictive model also addresses the aspect of evolution of the binder's stiffness as a function of time in order to reflect the performance related properties of the chip seal.

The previous discussions have also highlighted the importance of the emulsion's rheological properties for chip seal applications. It was pointed out that premature failure of chip seal applications can sometimes be attributed to non-conformance to the agency's specifications for the particular material. The illustrations and examples cited above indicate the need for development of a test method that can be employed at the project site to determine the characteristics of the emulsion as well as its suitability for construction. In addition, such a test could also serve as a tool to assess whether or not

the emulsion is partially broken when delivered to the construction site. Therefore, the third and final objective of this study includes the investigation of the use of electrokinetic techniques to develop a rapid portable test method that measures breaking characteristics of an emulsion.

Thus, to summarize, the work carried out for this part of this research study addresses issues pertaining to timing of placement of aggregates and waiting period before a newly constructed chip seal is open to traffic. In addition, the breaking characteristics of asphalt emulsions in an electric field were studied in order to develop a fundamental understanding of the breaking characteristics of the emulsion using electrokinetics. This latter part further aided in the development of a test procedure that can be used for quality control and quality assurance by field inspectors and engineers alike.

1.5. ORGANIZATION

This document summarizes the work that has been carried out as part of this dissertation. It is subdivided into five chapters, with the first one introducing the reader to asphalt emulsions and its use in the construction industry, providing a background aimed at identifying the current state of practice and the lack of a formal procedure regarding the use of asphalt emulsions in the paving industry. This would help the reader realize the research needs and therefore the objective of this study. The second, third, and fourth chapters summarize the results and the methodology adopted in addressing the objectives identified as part of Chapter 1. The final chapter summarizes the findings of this study,

highlights scope for future research and provides a synopsis of the overall contribution of this research work.

Chapter 2: Modeling of Curing Rates and Determination of Optimal Timing for Placement of Aggregates

2.1. The Role of Environmental Factors in the Curing Rates of Asphalt Emulsions

Emulsions used on surface treatment application generally have a residual asphalt content ranging between 60 to 70%. Consequently, the emulsion is sufficiently viscous at ambient temperatures which prevent it from flowing when applied onto the pavements surface with a cross-slope. However, the preferred application temperature is kept above 55°C. The higher temperature allows the emulsion to be sprayed without clogging the nozzles, to be spread faster and cool more rapidly when it comes in contact with the pavement surface and thus prevents drain-off. Therefore, the amount of water lost to evaporation before the aggregates are spread, occurs in two stages: first while the emulsion cools down from the application temperature to ambient conditions which is then followed by normal evaporation due to convectional heat transfer at ambient temperature.

The total amount of evaporative water loss can be modeled as follows:

$$M_{tot} = M_{cool} + M_{con} \quad 2.1$$

where,

M_{tot} : Total amount of moisture lost

M_{cool} : Amount of moisture lost while the emulsion comes to a thermal equilibrium with its surroundings

M_{con} : Amount of moisture lost due to absorption of latent heat of vaporization by the emulsion from its surroundings

The following section discusses the empirical approach that was adopted for modeling these two different modes of moisture loss from an asphalt emulsion.

2.1.1. Loss of Moisture due to Cooling of the Emulsion

Emulsions are generally applied at temperatures around 60°C. In most cases, the applied emulsion will exchange heat with the surrounding environment and during this process the water in the emulsion will absorb the latent heat of vaporization from the internal energy of the system; thus lowering its temperature further. The kinetics of the cooling process will depend upon the specific heat capacity of the air and the temperature gradient between the emulsion and its surroundings. The total amount of water vapor that can be generated will be limited by the amount of water that the emulsion had as part of its original formulation. It has been pointed out in the foregoing discussion that the evaporation of water from the emulsion is controlled by the rate of diffusion of the vapor through the asphalt phase as the emulsion starts to break and from a continuous phase. The diffusion barrier will continue to evolve with time as the emulsion breaks and cures which will eventually hinder the evaporation of water from the emulsion. Thus the rate of evaporation of water will gradually slow down. The total amount of moisture lost while the emulsion is cooling can be modeled as a series of incremental time intervals where each of the intervals can be characterized by:

- The temperature specific to the time interval, which will be lower than its temperature in the previous time interval due to the cooling process, and
- The amount of water present in the emulsion, which will also evolve with time due to continuous removal of water from the system due to evaporation

According to the framework of the problem described above, the temperature during the first time interval will be equal to the application temperature for the emulsion and the amount of water in the system will be equal to the water present in the original formulation of the emulsion. Given that the convective heat transfer coefficient of air (k) is known, the duration of this process can be determined using Newton's law of cooling (Winterton, 1999). The total amount of water that will be lost through evaporation during this time interval will be governed by the temperature, humidity and turbulence (represented by wind speed) in the surrounding environment. The temperature profile given by Newton's law of cooling can be used to define the system states at any time. The rate of evaporation at different system states is defined by the temperature and the humidity for that state which can be obtained from experimental data. Together with the temperature profile obtained from Newton's law of cooling, the evaporation rate determined at different states can be integrated over the duration of this process to compute the total amount of water lost while the emulsion cools down to the ambient temperature.

It should be noted in this context that "k" is dependent on the type of media, gas or liquid, the flow properties such as velocity, viscosity and other flow and temperature dependent properties and therefore needs to be determined for asphalt emulsions from laboratory tests.

2.1.2. Loss of Moisture due to Vapor Pressure Deficit

Evaporation is the transformation of liquid water into a gaseous state and its diffusion into the atmosphere (Davie, 2008). The evaporation cycle requires two basic elements:

the availability of water and the availability of energy. The main sources of energy for evaporation come from the sun in the form of incident radiation and heat waves re-radiated from other surfaces. In addition, the atmosphere should be dry enough to receive any water vapor produced. Dalton was the first to propose a model connecting wind speed and dryness of ambient air to the evaporation rate (Ward et al., 2004).

According to Boyle's law, the total amount of water vapor that a definite volume of air can carry is temperature and pressure dependent. This implies that for a given temperature and air pressure, it is possible to determine the maximum amount of water vapor or saturation vapor pressure that a given volume of air can carry. Mathematically, the saturation vapor pressure can be calculated as:

$$e_s = 0.6108 e^{\frac{17.27T}{T+237.3}} \qquad 2.2$$

where,

e_S : Saturation vapor pressure in kPa, and

T : Ambient temperature in ºC.

By quantifying the ambient and saturation vapor pressure, one can estimate how much more water vapor the air can take until it reaches saturation. The difference between the ambient and saturation vapor pressure is the vapor pressure deficit (VPD). The amount of water vapor that can escape from an evaporative surface has a direct relationship with the vapor pressure deficit. Therefore, the higher the vapor pressure deficit, the higher the potential loss of water due to evaporation. Mathematically, the vapor pressure deficit can be expressed as follows:

$$VPD = e_s\left(1 - \frac{RH}{100}\right) \quad 2.3$$

Where,

VPD : Vapor pressure deficit, and

RH : Relative humidity in percentage.

The other component of the evaporative relation is the rate of atmospheric mixing, which indicates how rapidly the given volume of air can diffuse into the surrounding atmosphere. *"The best indicator of atmospheric mixing is the wind speed at different heights above an evaporating surface"* (Davie, 2008). If there is no turbulence in the air above the evaporative surface, sooner or later the air will get saturated with water vapor, which will stall the evaporation process. On the contrary, higher wind speeds promote atmospheric mixing and result in drier air replacing the moist air blanket over the evaporation surface. Meyer's empirical formula, which is based on Dalton's law, is used to estimate the evaporation from open water surfaces (Ward et al., 2004). Meyer's formula accounts for the atmospheric mixing component of the evaporation equation through the following expression:

$$E = C \times VPD\left(1 + \frac{u_{25}}{10}\right) \quad 2.4$$

Where,

E : Amount of moisture loss due to evaporation,

VPD : Vapor pressure deficit in inches of Mercury,

C : Empirical constant that depends on the nature of the water surface, and

u_{25} : Average wind speed in mph at a height of 7.6 metres (25 feet) above the evaporative surface.

Meyer's equation includes a term to estimate the atmospheric turbulence and rate of diffusion of the ambient air. The equation integrates all the weather parameters into one single expression that could be used to predict the evaporation rate. However, the focus of this study is to model the amount of evaporative water loss as a function of time and weather conditions until the chips can be spread. The amount of water that can evaporate from the emulsion sample is therefore limited to the total amount of available water in the system. As the Meyer's equation was originally developed to predict the evaporation from open water surfaces, it had to be calibrated first. In this study, the equation was calibrated with experimental data obtained from the weathering racks, shown in Figure 2.1. The racks, almost 1.2 metres above the ground, were exposed to atmospheric conditions. A sample size of 30 grams with a film thickness of 2 mm was used for this part of the study. The application rate was decided after considering the typical application rate for emulsions for seal coat jobs (0.45 gallons per square yard for Grade 4 aggregates) in Texas. Samples of emulsion where placed in pans and placed on the weathering racks.

Figure 2.1: TxDOT Weathering Racks and the Measurement of Evaporation Rates

The model that was developed as part of this research uses the Meyer's equation as a fundamental basis for developing a relationship between the weather parameters and the rate of evaporation. The model was adjusted to take into account the differences that exist between an open water surface and an emulsion sample.

In addition, water in the emulsion has to diffuse through the emulsion film to the surface in order to evaporate. It should also be noted in this context that as the water leaves the system, the emulsion undergoes a phase change from a liquid to a solid state (the residual asphalt binder) and therefore the phase front is dynamic in nature. Thus the problem in hand is a classic example of the Stefan's problem which involves studying processes involving phase transformation of the matter (Budak et al., 1965). However, the wait time for placement of aggregates in the field is in order of 5 to 15 minutes.

Evaporation is a surface phenomenon and therefore the vaporization of water will be confined mostly to the liquid-gas interface. As the water evaporates, the asphalt cement residue will be left over as a thin membrane, the process is often referred to as *"skinning"*. Thus there is a gradual transformation from liquid to solid phase and the formation of skin on the surface implies that the evaporation of water is now diffusion-controlled due to the fact that the water has to first permeate through the skin to reach the liquid-gas interface. The modeling of evaporation of water at this stage requires knowledge of diffusion rates through the asphalt cement and also the rate at which the thickness of the skin grows over time. Instead of measuring these critical parameters, the evaporation of water was measured at regular time intervals and was modeled using a sigmoidal equation which factors in the different forces that affect the rate of evaporation of water including the effect of skinning.

2.2. MEASUREMENT OF CURING RATES IN THE LABORATORY

2.2.1. Laboratory Results

To evaluate the rate of evaporation as the temperature of the emulsion changes while it cools, it is important to develop an experiment that can help quantify this rate. A mass loss experiment using the Thermo-Gravimetric functionality on a Differential Scanning Calorimeter with Thermo-Gravimetric Analyzer (DSC/TGA) from Thermal Analysis (TA) instrument was conducted under isothermal conditions. The Thermo-Gravimetric functionality determines changes in weight in relation to change in temperature. The goal was to determine the rate of vaporization of water under different temperature regimes, so the test was conducted at seven different temperatures ranging from 50°C to 80°C. Figure

2.2 shows the rate of moisture loss from a 3.5 gram sample of CRS-1P (i.e. cationic rapid-setting emulsion with low viscosity, polymer modified) emulsion sample at each of these seven different temperatures.

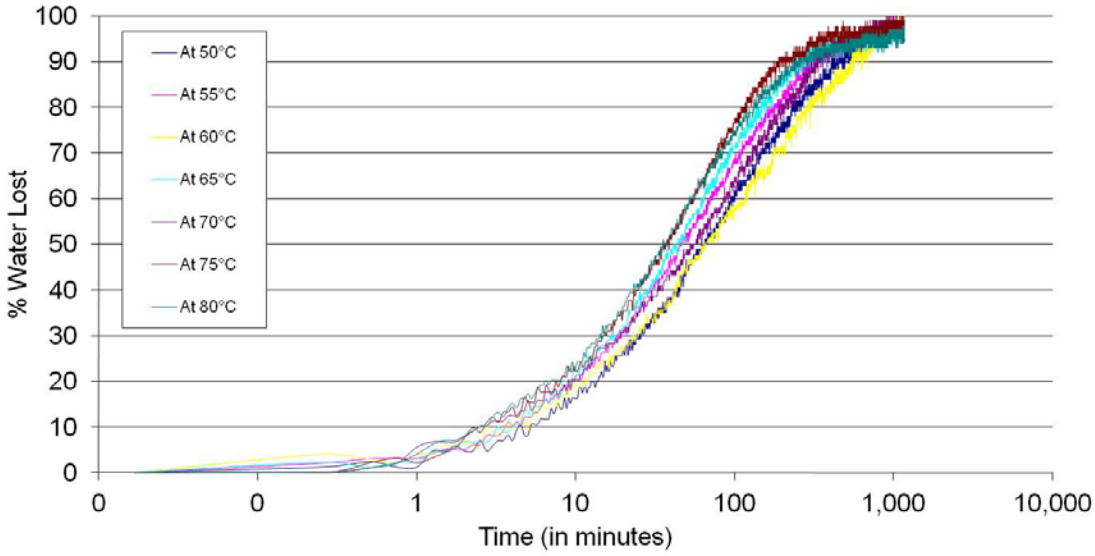


Figure 2.2: Evaporation vs. Time for a CRS-1P Emulsion at Different Temperature Profiles

The sample mass was confined between 3.2 and 3.5 grams in order to keep the measurements consistent. To quantify the amount of moisture lost after the emulsion reaches a state of thermal equilibrium with the surroundings, a different approach was adopted. Weathering racks were used as the reference standard to cure the asphalt emulsions. The evaporative water loss was typically measured 3 to 4 times during the first 6 hours as the emulsion was exposed to atmospheric conditions. It should be mentioned that the sole purpose of this part of the study was to determine the optimal time to put down the aggregates in the field and, therefore, the experiment was conducted without bringing any aggregates in contact with the emulsion. Typically, the aggregates

are placed between 3 to 15 minutes from the time the emulsion is sprayed. Under the scope of this study, the evaporation rates were measured for a period of 6 hours in order to obtain sufficient information on the rate of evaporation during the initial as well as after the skin formation are observed. The specific emulsions included as part of this study to determine the rate of curing are as given below.

- CRS-2P (Viscosity: 195 Saybolt Furol Seconds (SFS), 94 penetration units (PEN))
- CRS-2 (Viscosity: 210 SFS, 143 PEN)
- HFRS-2 (Viscosity: 162 SFS, 108 PEN)
- HFRS-2P (Viscosity: 173 SFS, 96 PEN)
- CRS-1P (Viscosity: 78 SFS, 292 PEN)

Where, “C” stands for Cationic, “RS” stands for Rapid Setting, “2” stands for High Viscosity, “1” stands for Low Viscosity, “P” stands for Polymer Modified, and “HF” stands for High Float.

Figure 2.3 shows the residual weight for a CRS-2 emulsion sample recorded on the weathering racks over a period of one week.

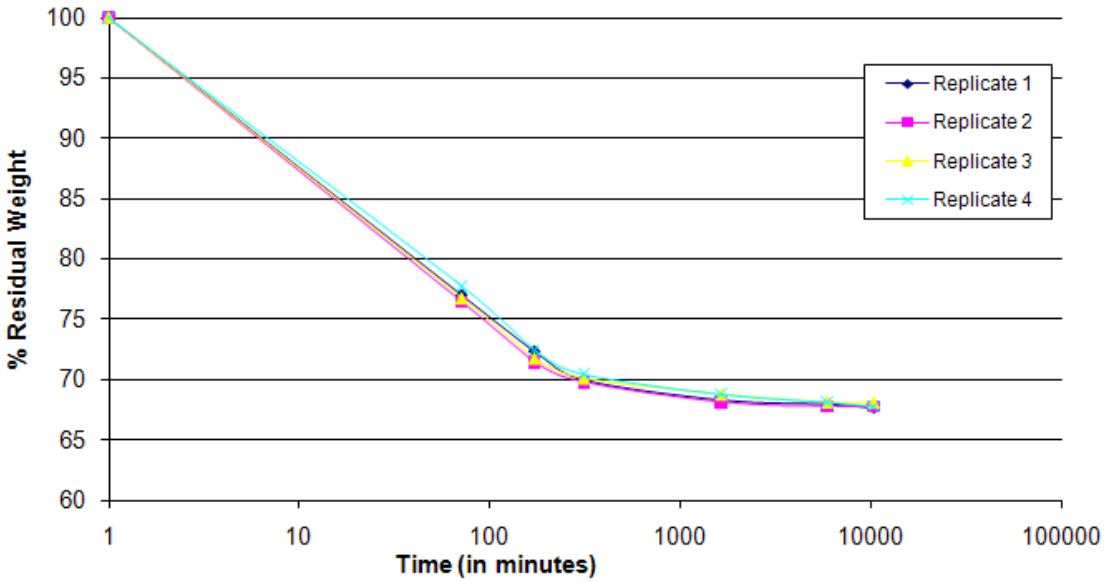


Figure 2.3: Mass Loss Measurements for a CRS-2 emulsion sample

A weather station was installed for meteorological monitoring at the testing location. The weather station was configured to report the following weather parameters at five minutes intervals:

- Temperature data in °C
- Relative humidity in percentage
- Solar radiation in kW
- Wind speed in mph
- Precipitation in inches

2.2.2. Modeling Evaporative Water Loss

Experimental data on the rate of evaporation of water from emulsion shows evidence that the rate of water mass slows down with time. This drop in the rate of evaporation can be

attributed to phase transformation as well as the decrease in the amount of moisture available in the system. The rate of evaporation can, therefore, be modeled using a time dependent relation as given below.

$$\frac{dm}{dt} = k_T \times m^{\beta} \qquad 2.5$$

Where,

dm/dt : Instantaneous rate of loss of water with respect to time,

k_T : Evaporation rate at temperature T (non-dimensional)

m : Amount of water present in the system with respect to original water content of the emulsion

β : Experimental constant

Ideally, one would normally expect the evaporation rate (k_T) to increase with increasing temperature as the energy input to the system is being raised. As the measurement of evaporation rates was conducted under seven different temperature profiles, it was possible to develop a relationship between evaporation rate and the temperature, as follows:

$$k_T = f(T) \qquad 2.6$$

The function f(T) can be utilized to determine the evaporation rate for any given temperature. Once the exponent and the evaporation rate are known, it is possible to determine the amount of evaporation from the emulsion subjected to any temperature profile, given that a continuous measurement of the temperature and the type of the emulsion are known. It should be noted that different emulsions react differently when

exposed to the same condition and, therefore, the evaporation rate should be determined separately for each of these emulsions. By discretizing Equation 2.5 into finite time or temperature intervals, the total amount of evaporation of water while the emulsion cools down from its application temperature can now be represented using the expression given below.

$$M_{cool} = m_0{}^{\beta} k_{T_0} \Delta t_0 + m_1{}^{\beta} k_{T_1} \Delta t_1 + \cdots \quad 2.7$$

$$\text{or, } M_{cool} = \sum_{n=T_i}^{n=T_f} \Delta t_n m_n k_{T_n} \quad 2.8$$

where,

T_i : Initial temperature of the system (application temperature)

T_f : Final temperature of the system (ambient temperature)

However, it has to be remembered that a higher energy input would accelerate the process of evaporation at early stages but it might at the same time inhibit the evaporation rate due to a faster skin formation due to the phase change phenomenon discussed previously. For example, a higher temperature will accelerate the loss of water from the surface layer than what it would have at a lower temperature. On the other hand, a slower evaporation rate will retard the rate of transformation of the liquid emulsion to the solid asphalt binder which will actively influence the rate of diffusion. Diffusion is faster in liquids than solids due to their higher degrees of freedom (Dickinson et al., 1999). Thus the transformation of liquid to solid phase will retard the rate of evaporation from the sub-surface layers of the emulsion. Together these two forces (the faster rate of evaporation and slower diffusion rates with increasing temperature or vice versa) will

compete against one another to define the final rate of evaporation in the emulsion. As a result, for the emulsion evaluated, the data did not show any significant increasing or decreasing trend in the rate of evaporation with increasing temperature, i.e. constant k_T. This suggests that the rate of evaporation reaches a maximum at an intermediate temperature and then the skinning controls the rate. In fact, the experimental data collected on the CRS-2P emulsion also supports the hypothesis. However, for other emulsions like the HFRS-2, the rate of evaporation decreases with increasing temperature which could support the same hypothesis as above, i.e. decreasing k_T, the difference being in the limits of the temperature range. With the CRS-2 emulsion, an opposite trend was noticed where the k_T steadily increases with increasing temperature. This can be due to the fact that the k_T reaches a peak at a temperature higher than 80°C and decreases for temperatures higher than the particular value.

The experimental data also provided evidence to support this hypothesis. The model parameters were estimated using linear regression and the results are summarized in Table 2.1.

k_T @	CRS-2P	CRS-1P	HFRS-2	HFRS-2P	CRS-2
50°C	0.0127	0.0155	0.0125	0.0147	0.0147
55°C	0.0132	0.0212	0.0117	0.0108	0.0165
60°C	0.0135	0.0161	0.0128	0.0078	0.0294
65°C	0.0158	0.0239	0.0133	0.0108	0.0398
70°C	0.0126	0.0213	0.0115	0.0082	0.0353
75°C	0.0113	0.0286	0.0136	0.0063	0.0413
80°C	0.0104	0.0301	0.0211	0.0062	0.0523
Average	0.0128	0.0224	0.0138	0.0093	0.0328
β	2.13	2.08	2.44	2.14	1.92

Table 2.1: Estimation of the Evaporation Rate

It can be seen from the results presented in Table 2.1 that the rate of evaporation varies proportionally with the square of the amount of water present in the system (i.e. $\beta \approx 2.0$). On the contrary, the coefficient of evaporation (k_T) increases or decreases as the temperature varies, depending on the type of emulsion. Due to lack of any systematic trends in the data, an average value of k_T was computed and its temperature dependency was ignored for the rest of this study.

Once the emulsion has cooled down and has reached a state of thermal equilibrium with its surroundings, the rate of evaporation is governed by the deficit in the vapor pressure (VPD) in the surrounding air. The process can be divided into a finite number of small time intervals where the amount of water lost during each of these time

intervals will be a function of the VPD. By definition, VPD will be a dynamic factor that will evolve with changing weather conditions as will the amount of water that will evaporate during each of these time intervals. As already mentioned, the mass loss measurements were recorded at finite time intervals that ranged between one and three hours. It can be reasoned that the total amount of water vapor lost from the system will actually be a summation of the water vapor lost during each of these small time intervals. This implies that in order to model the amount of evaporative water loss, it is essential that the integral of any time-dependent parameter is calculated in the model.

It is important to choose a suitable empirical form for the model such that its values are constrained within physically reasonable bounds. The empirical form of the model chosen for this study is as given below.

$$\mathrm{M_{con}} = 100\left(1 - \mathrm{e}^{-(\beta_0+\beta_1 \mathrm{E})}\right) \qquad 2.9$$

where,

M_{con} : Total amount of water evaporated as a result of VPD in the ambient air

β_0, β_1 : Regression parameters

E : Product of Vapor Pressure Deficit (in kPa) and wind speed (in mph)

The regression coefficients are given in Table 2.2.

F-statistic		18.63	
Adjusted R-Square		0.64	
Number of Observations		53	
Effect	Coefficients	t-statistic	p-value
Intercept (β0)	0.89	3.6	0.002
E: Product of VPD & Wind Speed (β1)	0.23	4.3	0.000

Table 2.2: Model Statistics and Regression Coefficients

The vapor pressure deficit and the wind speed data were obtained from the weather station that was deployed in this study. The temperature, relative humidity and the wind speed data were monitored at 5-minute intervals and were, then, integrated over the duration of the experiment and used for modeling the curing rates. The analysis of the results reveals that the curing rate of the emulsion is positively correlated to the product of the vapor pressure deficit and wind speed. This is indicated by the high t-statistic in Table 2.2, i.e. 4.3. A higher vapor pressure deficit implies a higher potential for the ambient air to absorb more water vapor while a higher wind speed translates to more vigorous atmospheric diffusion of the water vapor in the surrounding mass of air.

2.3. FIELD VALIDATION AND DETERMINATION OF THRESHOLDS

In order to properly develop a protocol for determining the waiting period before aggregates can be placed in a chip sealing job, it is essential to know the optimal amount of curing an emulsion must go through so that it can withstand the shear stresses to prevent aggregate loss. Given the limited timeframe from the time the emulsion is

sprayed to the time when the chips are placed, it is difficult to measure the amount of water loss with a reasonable degree of accuracy. The alternative can therefore be to estimate the amount of water loss that the emulsion will go through until the aggregates are placed. In order to satisfy the needs of the problem, one should collect weather conditions which will include temperature, humidity and wind speed – sufficient to determine the amount of moisture loss due to the vapor pressure deficit and the atmospheric turbulence in the surrounding air. The other half of the effort should be directed towards gathering information on the rate of thermal cooling in the asphalt emulsion from the moment it is sprayed on the pavement along with simultaneous measurements of the meteorological parameters. Given that this information is available, one can use Newton's law of cooling to determine the time before the emulsion reaches a state of thermal equilibrium with the surrounding environment. Table 2.3 summarizes project related information that was collected during the field validation phase of the study. The purpose of the field evaluation study was to look at the typical waiting period before the aggregates are placed at construction job sites under varying conditions. Type of emulsion, geographical region and the season were some of the variables collected. For example, field sites like Floydada and Plainview are located in North Texas which is relatively drier and cooler than sites like Giddings or Comanche which are in Central Texas. The construction job at Floydada was executed during the later part of the fall season while others like those in Giddings or Comanche were constructed during the hot summer months.

Location	Brackenridge	Plainview	Floydada	Giddings	Comanche
Type of Emulsion	CRS-2	CRS-2P	CRS-1P	HFRS-2P	CRS-2H
Spray Temperature (°F)	140	140	130	135	133
Mean Air Temperature (°F)	96.6	77.6	75.4	83.3	78.3
Time to reach Thermal Equilibrium (mins)	4	5	5	4	3
Time to put Aggregates (mins)	15:00	07:15	13:30	3:30	7:30
Convective Heat Transfer Coefficient (k)	0.0242	0.0288	0.0241	0.0285	0.0191

Table 2.3: Site-specific Measurements related to Curing Rates from Field Projects

Having measured the rate of temperature drop in the emulsion as a function of time, one can apply Newton's law of cooling to determine the rate of cooling and the time to reach thermal equilibrium. Newton's law of cooling states that the rate of change of the temperature of an object is proportional to the temperature differential between the object and the surrounding environment (Winterton, 1999). Mathematically the process can be represented by the following differential equation.

$$\frac{dT}{dt} = -k(T_o - T_a) \qquad 2.10$$

Where,

dT/dt : Rate of Change of Temperature w.r.t Time

T_0 : Temperature of the object

T_a : Temperature of the ambient air – held constant over the duration of the experiment due to the relatively small time interval.

Defining a new variable,

$$y(t) = T(t) - T_a$$

Therefore,

$$y(0) = T_0 - T_a$$

Differentiating w.r.t time,

$$\frac{dy}{dt} = \frac{dT}{dt} = -K(T - T_a) = -Ky$$

Solving the differential equation $-Kt = ln\left(\frac{y}{y_0}\right)$

$$or, y = y_0 e^{-Kt}$$

$$or, T - T_a = (T_0 - T_a)e^{-Kt}$$

$$or, T = T_a + (T_0 - T_a)e^{-Kt} \qquad 2.11$$

The convective heat transfer coefficient (K) was calculated using a least squares approach. The ambient air temperature (T_a), the spray temperature (T_0) and the instantaneous temperature T of the emulsion was recorded during the field trials. Knowing all the parameters in Equation 2.10, the observed data was fitted with the model using a least squares approach and the convective heat transfer coefficient was estimated. Given that the ambient temperature, the initial temperature of the emulsion and the instantaneous change in the temperature are known, the equation can be solved for the convective heat transfer coefficient to determine the rate of cooling. The heat transfer coefficient was determined from the project data that was collected. However, there was

some variability that was observed between the heat transfer coefficients determined for each of the field projects which led to the decision of using an average value of 0.0249 W/m^2K. Having determined the heat transfer coefficient, one can calculate the time taken by the emulsion to cool down and reach a state of thermal equilibrium as well as the amount of water that will be lost during this time interval. Once the emulsion cools down to the ambient air temperature, the amount of water that will be lost henceforth will be determined by the vapor pressure deficit of the ambient air which can be determined by the model presented in Table 2.2. The amount of water lost before the aggregates were placed was calculated for each of the field projects and the results are summarized in Table 2.4.

Location	Brackenridge	Plainview	Floydada	Comanche	Giddings
% Water Lost before Emulsion Cools down	14.2	8.1	10.2	14.2	3.0
% Water Lost after Emulsion Cools down	14.2	3.3	11.7	3.5	0.0
Total Amount of Water Lost before Aggregates are placed (%)	28.4	11.4	21.9	17.7	3.0
Average (%)	19.8				3.0

Table 2.4: Determination of the Percentage of Water Lost before the Aggregates were placed

The results in Table 2.4 vary quite a bit from one project to the other. However, if the results are segregated into two groups based on the type of emulsifier, the cationic emulsions follow a generic trend. On the contrary, the anionic emulsion exhibited a lower

percentage of water loss when the aggregates were placed. The apparent anomaly can be explained by the fact that the cationic surfactants have a relatively lower hydrophilic character (SFERB, 2008). This eventually results in faster breaking rates for cationic emulsions and a higher rate of moisture loss as compared to anionic emulsions.

Under the assumption that the time when the aggregates were placed at each of these projects was optimal (as no early failures were observed), it can be concluded that the amount of water that was lost was the required amount of moisture loss for providing adequate resistance to tire pickup during rolling. It should be noted that determining the threshold will require developing an experimental design where early failures should be observed. However, no highway agency will want to participate in a study where they will know a priori that some of the chip seals that will be constructed will fail prematurely. Keeping in mind all these possible constraints, it was decided that the average of the percent water that was lost until the aggregates were placed is the threshold for placement of stones. Thus the threshold for placing aggregates was proposed as 19.8% and 3.0% for cationic and anionic emulsions respectively. There may be arguments that the threshold for anionic emulsions is based on observations from a single job site which is definitely not enough. However, considering the decreasing popularity of anionic emulsions it has been difficult to get projects that met the requirements and thus, it is recommended that further effort in this direction is required to enhance the reliability of the proposed thresholds.

Chapter 3: Determination of Optimal Time to Open a Newly Constructed Surface Treatment to Highway Traffic

This subsection discusses a methodology to determine the optimal time to open a new chip seal to traffic. Analysis of the laboratory data was performed to determine how environmental conditions and material properties affect the rate of evaporative water loss as well as the evolution of the rheological properties of the emulsion residue. Thresholds for the proposed models were determined based on limited field studies that were conducted to determine the degree of setting necessary for satisfactory performance.

3.1. BACKGROUND

Loss of aggregates may be triggered by a number of factors such as improper timing of placement of emulsified asphalt or cover aggregates, lower than the desired application rate due to over dilution of the emulsion, and opening to fast traffic before proper adhesion is developed. However, it is believed that the underlying reason for loss of aggregates is due to inadequate development of the adhesive bond between the emulsified binder and the cover aggregate (Epps et al., 2001). It is therefore essential to estimate the breaking and curing trends for asphalt emulsions to be able to predict the strength characteristics of the paving material and, hence, the optimal time to open the newly constructed surface treatment to traffic.

Epps et al. (2001) reported that loss of aggregates or raveling at high and low temperatures were the primary failure mechanisms that were controlled, at least in part, by the binder properties. At high temperatures they hypothesized that loss of aggregates was triggered by the high shear stresses generated on the road surface under the action of

wheel loads. When these shear stresses exceed the shear strength of the asphalt binder, the wheel loads dislodge the aggregates from the road surface. The Performance Grade (PG) binder specification uses the term G*/sin δ as the high temperature parameter under the assumption that binders with lower amount of work dissipated in a load cycle (or higher G*/sin δ) would be more resistant to permanent shear deformation or rutting (Roberts et al., 1996). In the context of surface treatment binders, higher values of G*/sinδ would reflect higher resistance to shear deformation under the action of traffic loads. Recent studies have pointed out that the thin film of asphalt residue left behind from a fully cured emulsion is subjected to high levels of shear strains as soon as the surface treatment is opened to traffic (Redelius, 2006). Thus it is essential that the binder has developed adequate strain tolerance or stiffness to prevent aggregate loss due to moving wheel loads. Testing the emulsion residue in a dynamic shear rheometer (DSR) can simulate this particular form of distress provided that the test is conducted at high strain levels (Hanz et al., 2009). In a recent study, select parameters from a strain sweep test on a variety of emulsions were shown to have a strong correlation with the results from the ASTM D7000 sweep test (Kucharek, 2007) in which a surface seal is brushed repeatedly to evaluate aggregate retention.

Research studies have reported that the interfacial tension between the asphalt and water molecules actively contributes to the rate of setting in surface treatment applications (McClements, 2005). Other elements including interfacial viscosity, electro-kinetic and rheological properties of the emulsion govern its stability and breaking characteristics. Most of this information is proprietary to the manufacturer and therefore a

mechanistic treatment of the problem is infeasible as part of this dissertation. Given these constraints, an empirical approach was adopted wherein the breaking and setting characteristics of the material were studied under controlled environmental conditions. This would facilitate the author to model the properties of the material and their evolution as the emulsion breaks down and eventually sets to deliver the final product.

3.2. EXPERIMENTAL DESIGN

In order to achieve the objectives, a carefully designed experimental plan was devised for the study which included running a mass loss test parallel to shear testing on the rheometer. While a mass loss test has the potential to capture the curing and setting characteristics of the emulsion, shear testing provides an insight into the evolution of the rheological properties of the binder. The advantage offered by running these two tests lies in the ability to correlate the results of one with the other as well as using a simple mass loss test as a surrogate for shear testing. To put things in perspective, the shear testing characterizes the performance properties of the binder but requires a controlled environment which confines it within the perimeters of the laboratory. On the contrary, a mass loss test does not provide information on the performance characteristics of the binder. However, its strength lies in its simplicity, portability, ease of execution and the ability to provide a measure of the amount of curing.

The experimental variables that were investigated as part of this study are as given below:

- Sampling Time : 2 hours, 6 hours, 24 hours and 48 hours
- Curing Temperature : 25°C (77°F) and 42.5°C (109°F)

- Type of Aggregates : Limestone Grade 4, Quartzite Grade 4, Light Weight Grade 4, No Aggregates
- Type of Emulsion : CHFRS-2P, CMS-1P, CRS-2, CRS-2P, HFRS-2 & HFRS-2P
- Replicates : 2

3.2.1. Sample Preparation

Sample preparation is one of the most crucial aspects of an experimental study as repeatability and consistency of measurements depend on the steps followed during this step. As for this study is concerned, the process involved the following steps:

- The emulsion is heated to 60°C (140°F) in a closed container to minimize evaporative loss. A sample size of 30 grams is poured onto a flat pan with a diameter of 140 mm giving a film thickness of approximately 2 mm, simulating typical application temperatures and application rates (300 l/m^2) characteristic of field projects.
- In the following step, the cover aggregates are added to the emulsion after waiting for 5 minutes from the time the emulsion was applied. The aggregates were pre-washed and oven dried before they were added to the emulsion. Typical stone application rates for limestone and quartzite aggregates were chosen as 4 kg/m^2 and that for light weight aggregates it was about 3 kg/m^2.
- The curing profile of the emulsion was recorded at 2 different temperature-humidity regimes: 42.5°C and 16% RH (Relative Humidity), and 25°C and 57% RH. It is to be noted that there were mild variations from the targeted values because of loss of

moisture from the sample. Given the relatively small size of the sample compared to the control volume, such effects were neglected.

- The sample weights were recorded at time intervals of 2, 6, 24 and 48 hours as part of the mass loss test. Sample preparation for shear testing normally requires reheating and molding of the specimen according to the dimensions of the test plates being used on the rheometer. However, the binder in question involves a partially cured emulsion sample, which if reheated will alter the sample, rendering it useless for the intended purpose. To avoid this problem, the author sampled directly from the test bed onto the lower plate of the rheometer. The shear tests on the emulsion samples were performed at 63°C to capture the in-field pavement temperatures typically observed in Texas. Furthermore, it allows cutting down the torque capacity of the instrument required for conducting the experiments. The shear testing on the rheometer was performed with 25 mm parallel plate geometry in a controlled stress mode on a Bohlin DSR-II Rheometer.

3.3. RESULTS

Figure 3.1 presents the mass loss measurements that were recorded in the laboratory for a CHFRS-2P emulsion sample. The two different sets of data (i.e. same color, different marker) represent the two different temperature-humidity profiles. The one setting faster represent the high temperature and low humidity regime and the other one representing the low temperature and high humidity combination. The color codes Blue, Yellow, Red and Black represents the Limestone, Quartzite, Light Weight and the control experiment ("No Aggregates" case) respectively. Furthermore, the suffixes "O" (see Figures 3.1 and

3.2) and “P” (see Figures 3.3 and 3.4) denote “Observed” and “Predicted” measures for the concerned parameter.

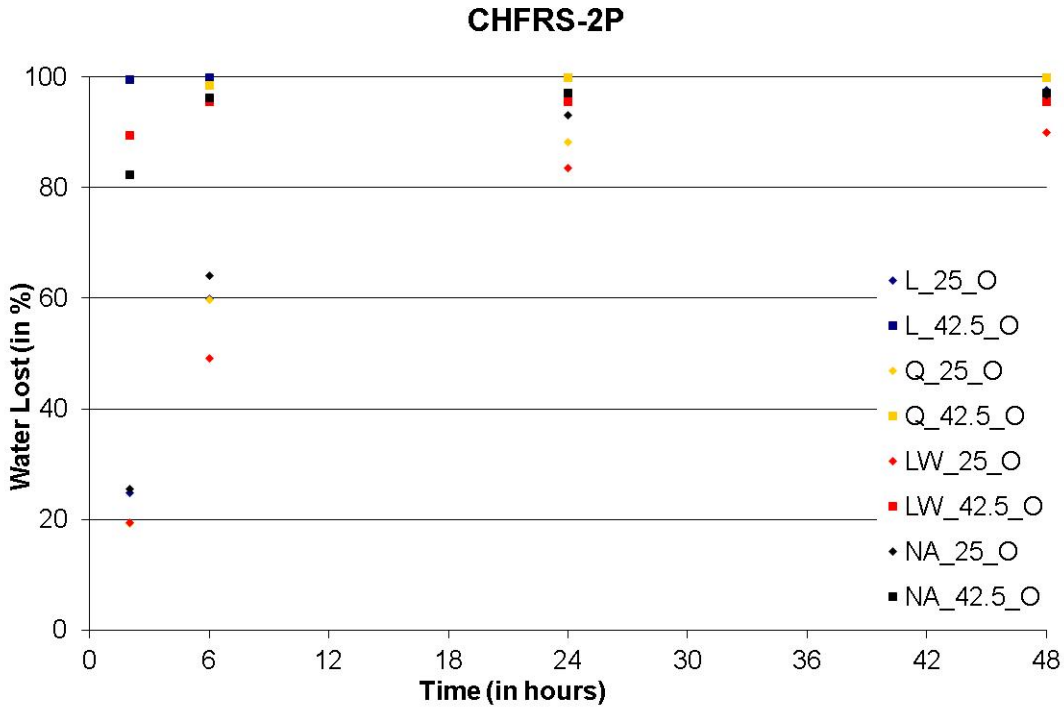


Figure 3.1: Evaporative Loss for different Aggregate-Temperature-RH Regimes for CHFRS-2P

It should be noted that the amount of water lost has been expressed as a percentage of the total water present in the system as part of the original formulation. As it can be seen from Figure 3.1, the setting characteristics of the emulsion depend on exposure conditions as well as the aggregate type. The trend in the data suggests that the choice of temperature-humidity regime heavily influences the rate of evaporative water loss. It is also evident from Figure 3.1 that the amount of water lost due to evaporation

reaches a plateau as it gets closer to 100% which is complete removal of water from the system.

Figure 3.2 presents the shear stiffness (G*) measurements at 63°C and 10 Hz for the emulsion residue recovered from a CHFRS-2P emulsion sample in the laboratory with the legends carrying the same significance as in Figure 3.1.

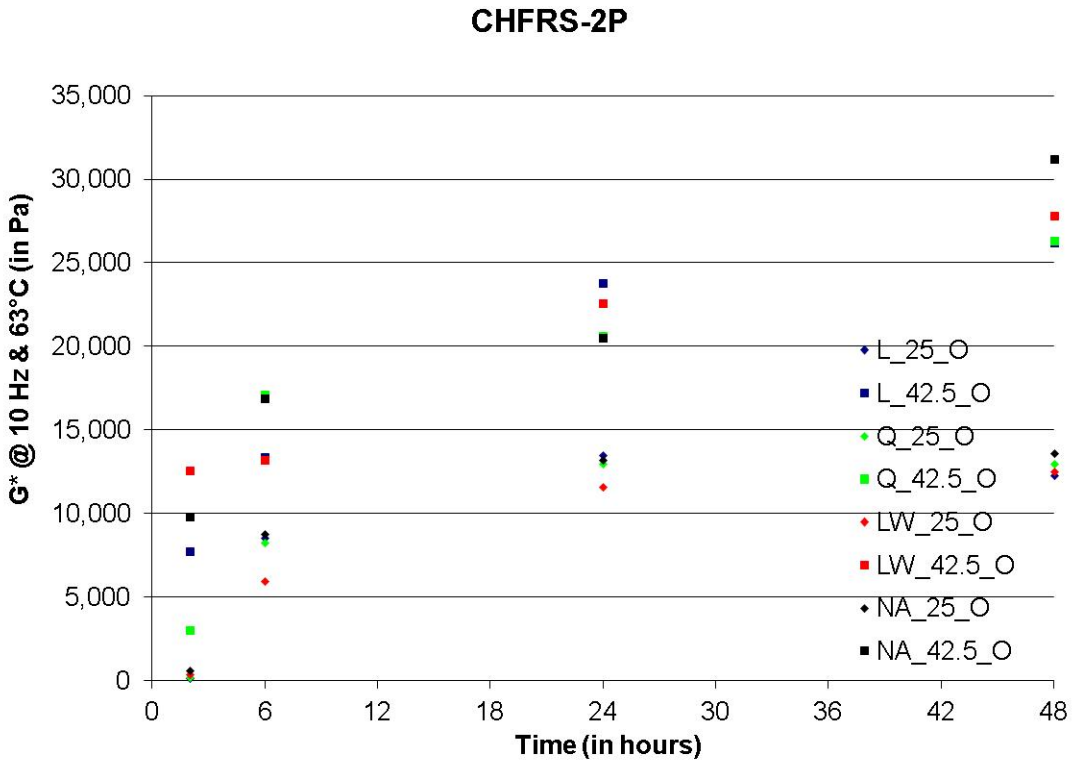


Figure 3.2: Complex Modulus of the Residue for different Aggregate-Temperature-RH Regimes for CHFRS-2P

It can be observed that the complex modulus of the residue fails to reach a plateau within the time period of the experiment. The stiffness of the residue increases as the emulsion cures and sets. However its stiffness continues to change due to aging of the

residual binder and this effect is more pronounced where the residual binder is exposed to a higher temperature.

3.4. DISCUSSION AND MODELING

One of the focus areas of this study involves investigating the rate of evaporation of water as the emulsion sets. The maximum amount of water that can evaporate in this scenario should be limited to the total amount of available water in the emulsion. However not all of the available water will have access to the evaporation front and thus the water present in the superficial layer will evaporate much faster as opposed to water present in the bulk of the emulsion. The formation of a superficial skin retards the rate of evaporative water loss which affects the dynamics of the process as the evaporation is partially diffusion controlled (Lesueur et al., 2002; Walter et al., 2002). Banerjee et al. (2012) have used vapor pressure deficit (VPD) to capture the influence of temperature and relative humidity on the evaporation of water from asphalt emulsions.

Studies have also shown that the mineralogy of the aggregates plays a major role in the breaking of emulsions and influences the setting characteristics of the emulsion (SFERB, 2008; James, 2006). The amount of water lost to evaporation can be modeled as a function of a set of covariates that includes weather conditions, emulsion and aggregate types. It is also important to choose a suitable empirical form for the model such that its values are constrained within reasonable physical bounds. After careful examination of the data trends, the empirical form of the model that was chosen for this study is given below:

$$y = 100\left\{1 - e^{\left[\left(\beta_0+\beta_1 Q+\beta_2 W+\beta_3 VPD+\beta_4 VPD\times\frac{CMS}{HFP}+\beta_5 VPD\times CRSP+\beta_6 VPD\times HF\right)x^{\beta_7 VPD+\beta_8 CMS+\beta_9 HFP+\beta_{10} CRS+\beta_{11} CRSP}\right]}\right\} \quad 3.1$$

Where,

y : % of water lost in a given interval of time

x : Interval of time (in hours)

β_0 *to* β_{11} : Regression Coefficients.

Q, W : Indicator variables corresponding to Quartzite & Light Weight aggregate types respectively (The absence of aggregates representing the reference scenario)

VPD : Average hourly vapor pressure deficit

CMS, HF, CRS, HFP, CRSP : Indicator variables corresponding to emulsions CMS-1P, HFRS-2 and CRS-2, HFRS-2P and CRS-2P respectively (CHFRS-2P being the reference emulsion type)

Table 3.1 summarizes the analysis that was undertaken as part of model development and highlights the statistically significant model parameters that influences the amount of water lost to evaporation. A total of 384 data points were used in developing the non-linear model presented in Equation 3.2.

Effect	Regression Coefficient	t-stat	p-value
β_0 (Intercept)	-0.183	-18.3	0.00
β_7 (VPD)	2.18	26.4	0.00
β_1 (Quartz)	0.0136	2.6	0.01
β_2 (Light Weight Aggregate)	0.0099	1.9	0.03
β_8 (CMS-1P)	0.0566	1.8	0.04
β_9 (HFRS-2P)	-0.0518	-1.9	0.03
β_{10} (CRS-2)	0.0434	1.6	0.06
β_{11} (CRS-2P)	0.313	7.8	0.00
β_3 (Intercept: VPD)	0.0344	4.5	0.00
β_4 (Intercept: VPD×CMS/HFRSP)	0.0226	3.5	0.00
β_5 (Intercept: VPD×CRS-2P)	0.0404	5.2	0.00
β_6 (Intercept: VPD×HFRS-2)	0.0725	3.2	0.00

Table 3.1: Model Parameters for Prediction of the Amount of Water Lost to Evaporation

It should be noted that the “Limestone” aggregates were dropped from the model as there was lack of evidence suggesting that the presence of limestone aggregates had a statistically significant effect on the evaporative water loss as compared to the reference scenario.

It can be observed from Equation 3.1 that the response and predictor variables are related through a nonlinear function which leads to a nonlinear regression model. Least squares estimation of the parameters in nonlinear regression is done through linearization

of the expectation function followed by Gauss-Newton iteration method. Linearization of the expectation function was accomplished using a first order Taylor series expansion.

Table 3.1 reports the statistically significant variables relative to the reference scenario (CHFRS-2P emulsion, no aggregates). As expected, the vapor pressure deficit affects the initial as well as the rate of moisture loss from the emulsion. Light weight and Quartzite aggregates were found to show a similar effect on the initial moisture loss which is indicative of faster breaking when the emulsion comes in contact with the aggregate surface (Reference scenario: No aggregates). In addition, the emulsions CMS-1P, CRS-2 and CRS-2P have faster setting rates compared to the reference case (CHFRS-2P) while HFRS-2P has a slower setting rate. The interaction between the vapor pressure deficit and the emulsion type had a positive influence on the rate of setting. For example, in the case of CMS-1P and HFRS-2P, the effect of VPD on the setting rate was more pronounced than any of the other emulsions. It should be noted that variables found statistically insignificant were dropped from the model. Therefore the final predictive model for determination of the amount of water lost due to evaporation from the emulsion will be as given below:

$$y = 100\left\{1 - e^{\left[\left(\begin{matrix}-0.18+0.014Q+0.01W+0.034VPD+(0.023VPD\times CMS/HFRSP)\\+0.04VPD\times CRSP+0.07VPD\times HFRS\end{matrix}\right)x^{2.18VPD+0.06CMS-0.05HFP+0.04CRS+0.31CRSP}\right]}\right\} \quad 3.2$$

The model fit with respect to the observed measurements from the laboratory has been provided for a CHFRS-2P emulsion in Figure 3.3.

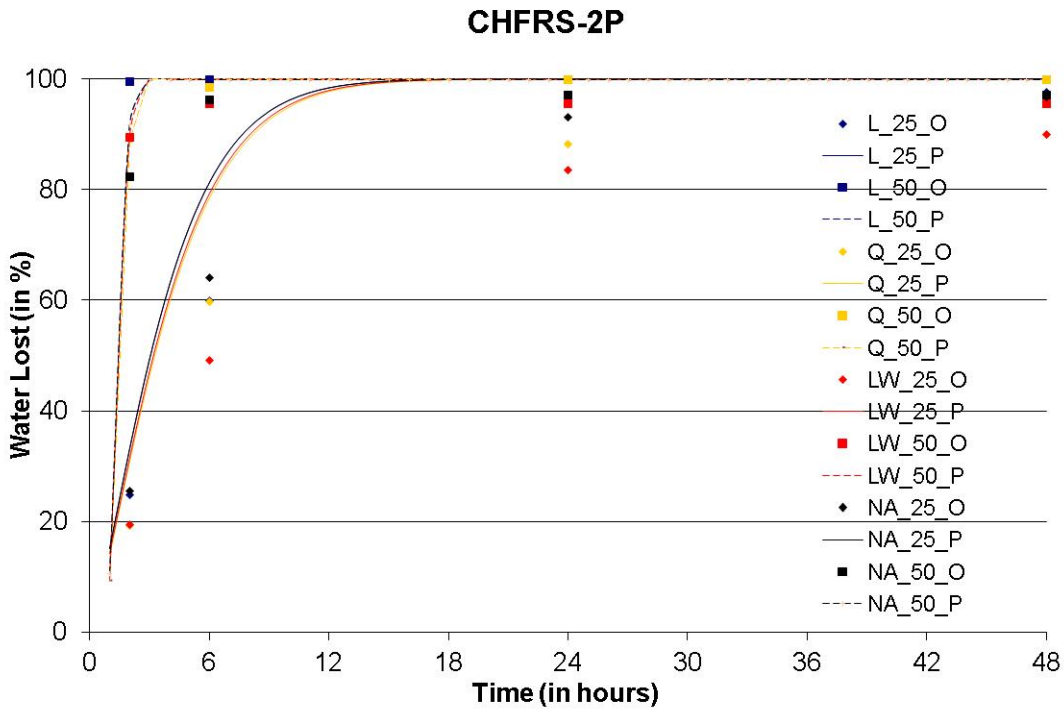


Figure 3.3: Observed V/s Predicted Water lost to Evaporation

The stiffness of the residue increases as the emulsion cures and sets. Furthermore, the shear modulus evolves due to aging and thixotropic effects of the residual binder which is more pronounced when the emulsion is exposed to the 42.5°C and 16% RH profile.

In determining the optimal time to open a newly constructed chip seal to traffic, it is absolutely necessary that the film of asphalt residue develops sufficient stiffness to resist high levels of deformation that results from dynamic traffic loads. The preceding

statement provides the background for modeling the stiffness of the residue as a function of changing weather conditions, time and material properties. Initial analysis of the data suggested that the stiffness of the residual binder increases as the emulsion sets due to the gradual loss of water and mild aging due to oxidation. Aging of binder is a continuous process, though its kinetics will be largely governed by temperature and pressure. Hence the stiffness of the residue fails to reach an asymptote which makes an exponential function inappropriate in the context of this problem. A power function was a relatively superior choice, given the trends observed in the dataset. The empirical form of the model is as given below:

$$y = (\beta_0 + \beta_1 L + \beta_2 Q + \beta_3 W + \beta_4 VPD + \beta_5 (VPD \times CHFP) + \beta_6 (VPD \times CRS) + \beta_7 CRS + \beta_8 (VPD \times CRSP)) x^{\beta_9 + \beta_{10}(VPD \times CHFP/CRSP) + \beta_{11} CRS + \beta_{12}(VPD \times CRS) + \beta_{13} CHFP/CRSP} \quad 3.3$$

Where,

y	:	Response variable (Stiffness, in Pa)
x	:	Interval of time (in hours)
β_0 *to* β_{13}	:	Regression coefficients
L, Q, W	:	Indicator variables for the aggregate types – Limestone, Quartzite & Light Weight
VPD	:	Average hourly VPD
CMS, CHFP, CRS, CRSP	:	Indicator variables for emulsions CMS-1P, CHFRS-2P, CRS-2 and CRS-2P

It should be noted here that the setting rate for the emulsion type HFRS-2P with no aggregate was considered as the reference scenario and therefore the regression coefficients capture the incremental change with respect to a residue obtained from curing of a HFRS-2P emulsion.

The model parameters for Equation 3.3 were estimated using nonlinear regression and the statistically significant parameters are summarized in Table 3.2. As it can be seen, that vapor pressure deficit has a positive effect on the initial stiffness gain in the emulsion while it continues to lose water but as such does not influence the rate of stiffness gain. Interactions between VPD and CRS-2P or CHFRS-2P have a positive influence on the initial shear stiffness of the emulsion residue while its effect subsides with time. Unlike what was observed for the setting model, the aggregates limestone and quartzite reduce the initial gain in the shear stiffness when compared against the baseline. Finally, the cationic rapid setting emulsions tend to gain stiffness faster than the anionic emulsions which can be attributed to the fact that the cationic emulsifiers have a lesser hydrophilic character than their anionic counterparts (SFERB, 2008).

Effect	Regression Coefficient	t-statistic	p-value
β_0 (Intercept [Baseline])	904	5.5	0.00
β_7 (Intercept: CRS-2)	1695	1.6	0.05
β_4 (Intercept: VPD)	320	3.7	0.00
β_5 (Intercept: VPD×CHFRS-2P)	2664.0	10.1	0.00
β_6 (Intercept: VPD×CRS-2)	-1272	-2.5	0.01
β_8 (Intercept: VPD×CRS-2P)	848.0	4.7	0.00
β_1 (Limestone)	-292	-3.0	0.00
β_2 (Quartzite)	-225.0	-2.5	0.01
β_3 (Light Weight Aggregate)	-94.9	-1.8	0.04
β_9 (Slope [Baseline])	0.484	9.8	0.00
β_{13} (Slope: CHFRS-2P, CRS-2P)	0.067	1.7	0.04
β_{11} (Slope: CRS-2)	-0.545	-3.0	0.00
β_{10} (Slope: VPD×CHFRS2P/CRS2P)	-0.093	-6.3	0.00
β_{12} (Slope: VPD×CRS-2)	0.395	3.8	0.00

Table 3.2: Model Parameters for Prediction of Stiffness of the Emulsion Residue

Although the experimental design lists six different emulsion types, the absence of an indicator variable corresponding to HFRS-2 in Equation 3.3 is due to lack of evidence suggesting that the residue recovered from the same will be any different from the reference scenario.

The standard error of the prediction was 2.5kPa, considered to be low after taking into consideration the differences that exist between the materials and exposure conditions. The final predictive model for determination of the stiffness of the residue is as given below:

$$y = (904 + 1695CRS + 320VPD + (2664VPD \times CHFP) - (1272VPD \times CRS) + (848VPD \times CRSP) - 292L - 225Q - 95W)x^{0.48-(0.09VPD\times CHF/CRSP)+(0.4VPD\times CRS)+0.07CHFP/CRSP-0.55CRS} \quad 3.4$$

The model fit with respect to the observed shear stiffness measured in the laboratory has been provided for a CHFRS-2P emulsion sample in Figure 3.4.

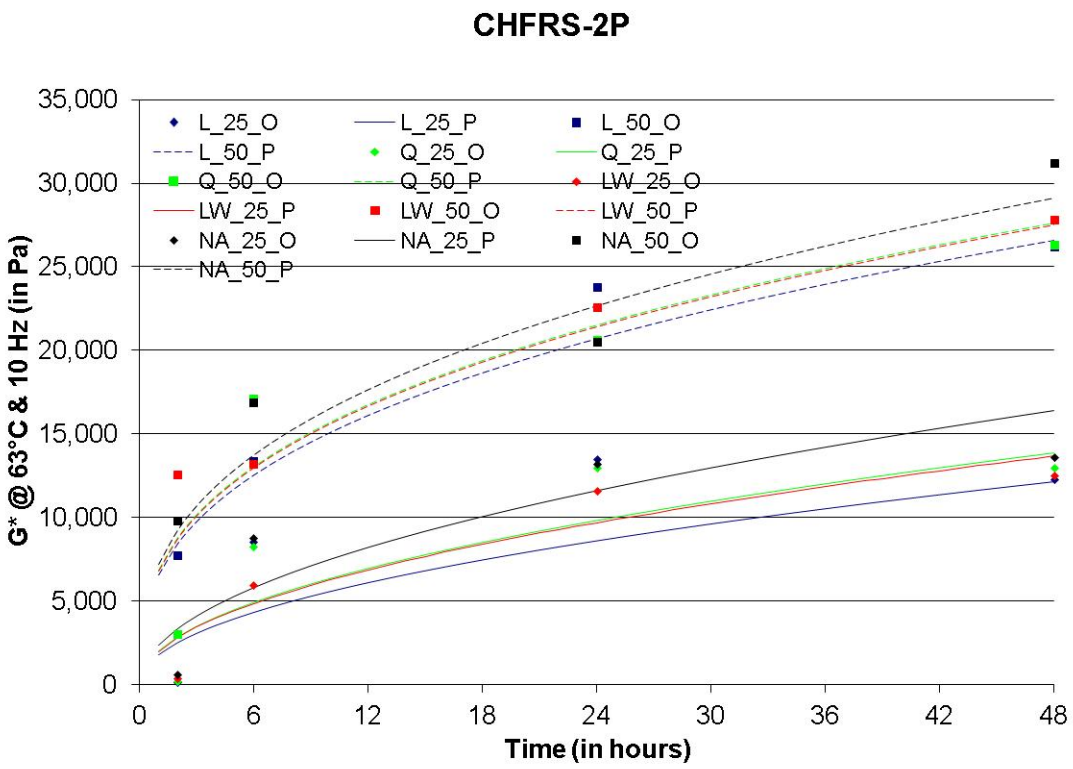


Figure 3.4: Observed V/s Predicted Stiffness of the Emulsion Residue

The model in its current form provides an excellent fit of the observed data for measurements recorded between 2 and 24 hrs. However, in general, one would not expect to wait longer than 24 hours to open a newly constructed chip seal and therefore for most practical purposes the statistical models discussed in this paper will give reliable estimates for opening to traffic.

3.5. Field Evaluation and Determination of Thresholds

One of the objectives of this study is to determine the optimal time to open the newly paved road to traffic. It is, therefore, imperative to determine the stiffness of the residue

and the amount of water that is lost before the newly constructed chip seal is opened to traffic. In order to meet this requirement, a field evaluation program was necessary to monitor the rate of setting of emulsions under field conditions.

Thin steel plates (see Figure 3.5.a) measuring 210 mm × 210 mm were placed on the road surface prior to construction of the surface treatment. To keep the experiment consistent with laboratory results, the area of coverage on the steel plates was kept equal to that of the Pressure Aging Vessel (PAV) pans (Ø = 140 mm) that were used for preparing the laboratory samples. The steel plates were put at 3 different stations 15 metres apart, with one plate on each of the wheel paths and one along the centerline of the lane – thus providing nine observations for each project that was included as part of the field evaluation study. The periphery of each of these plates was masked in order to have a consistent area of coverage throughout. The steel plates were removed from the road surface after two applications of the pneumatic rollers to ensure that the aggregates are properly seated in the emulsion and the masking paper was removed (see Figure 3.5.b). The sample of chip seal collected on the steel plate was allowed to set under ambient conditions which gave the closest possible replica of the newly paved chip seal. The particular exercise helped the author capture the setting characteristics of the newly paved surface treatment under field conditions and provided critical information pertaining to its in-situ rate of evaporation.

Figure 3.5: (a) Masked steel plates measuring 124mm × 124 mm (210 mm × 210 mm – Unmasked) (b) Final chip seal sample collected after two passes of the pneumatic rollers

Weight measurements were taken at regular intervals of 30 minutes for the first 3 hours and at 1 hour intervals thereafter, until constant mass. However, it should be noted that the rate of curing cannot be fully known until the amount of emulsion that was sprayed on each of these plates is known. To address the specific need, the field samples were stored in a dust free environment for a period of 14 to 21 days to ensure that all water had evaporated which implies that the combined weight of the sample is the sum of the asphalt residue from the emulsion and the aggregates. The samples are then exposed to high temperature in an ignition oven to determine the binder content for each chip seal sample. Dilution ratios for the emulsions were calculated using high temperature evaporative techniques which, when combined with the results from the ignition oven, can be utilized in back calculating the application rate and the rate of evaporation of water as the emulsion sets (see Figure 3.6).

Although the amount of water lost to evaporation can be quantified using simple field tests, it cannot provide information on the performance characteristics of the binder residue that is left from partial or complete curing of the emulsion. Additional testing in a laboratory environment was done to correlate the amount of curing to the stiffness of the emulsion residue. Weight loss and the shear modulus of the binder residue were measured at time intervals of 2, 6, 24 and 48 hours with the same emulsion and aggregate that was sampled from the project location. This allowed the author to construct a relationship that relates the amount of evaporative water loss to the stiffness of the residue (Figure 3.7).

In the field, the time taken to open the newly paved chip seal to traffic was also recorded for each of the projects which were included as part of the field monitoring program and the details are included in Table 3.3. The purpose of the field evaluation program was to establish the thresholds for the predictive models. In principle, the ideal situation will be to monitor a certain number of projects where early failures and successful cases are observed. However, this was not practical. Therefore, the thresholds presented henceforth are a conservative estimate. It was assumed that the time to open the chip seal to traffic was optimal under the given weather conditions and materials that were chosen for the project – based on the experience of the paving contractor and field inspector. However, this leaves room for further adjustments to the thresholds to determine the optimal timing for opening the road to traffic, if condition surveys are performed on these projects in the future.

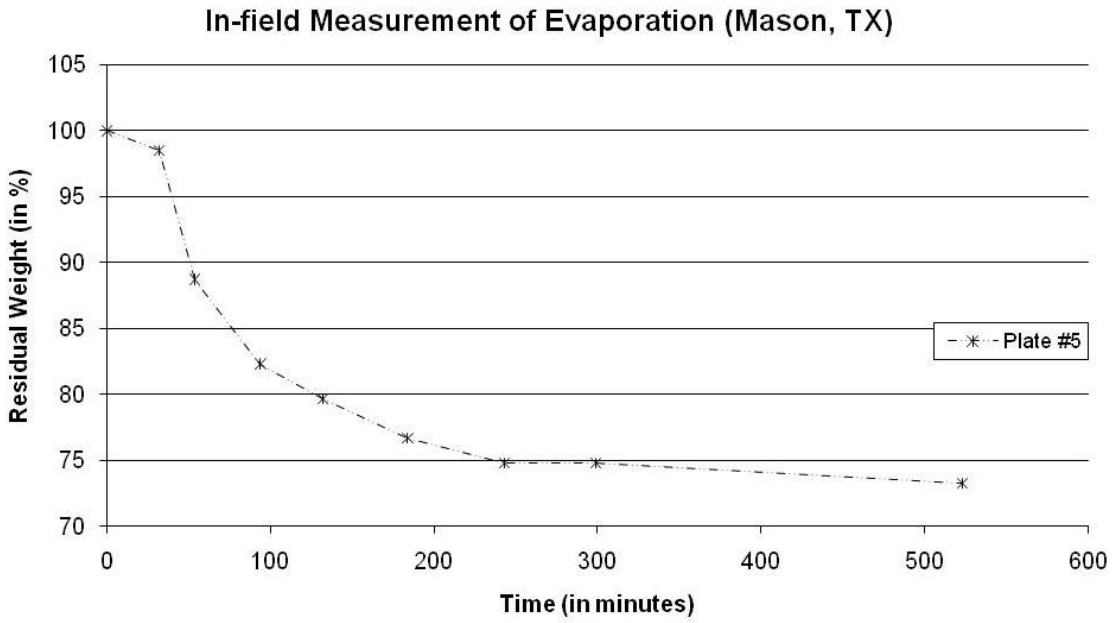


Figure 3.6: In-field Measurement of Evaporation Rate for Chip Seal Paving Job in Mason, TX

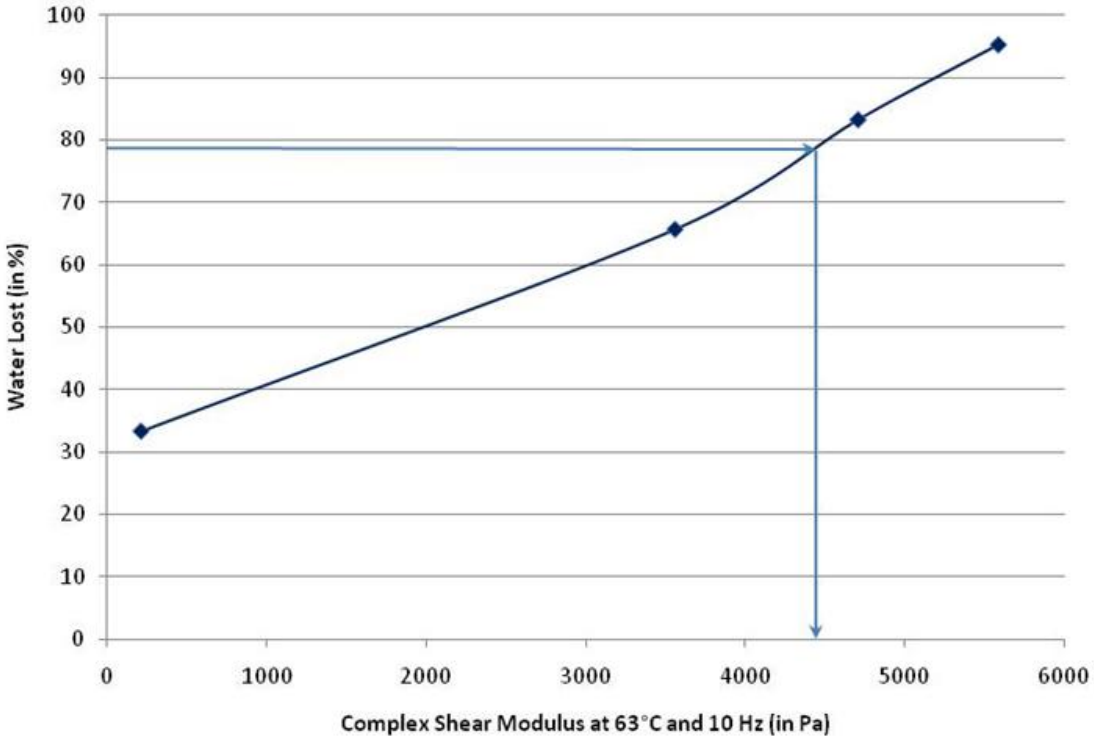


Figure 3.7: Evaporative Water Loss versus Complex Shear Modulus of the Emulsion Residue (CRS-2H with Limestone aggregates, Comanche, TX)

The optimal time to open the road to traffic is the time interval that is adequate to reach the required amount of water loss as determined during the field monitoring program. This threshold for water loss was calculated at 75.8% from the prediction model.

Field observations demonstrated that, for the same amount of relative loss in water, different aggregate-emulsion combinations yield shear moduli that are considerably different and therefore using an average of the stiffness from the different projects is not the ideal approach. Selecting the minimum stiffness as the threshold value would be the most appropriate choice as it will ensure that aggregate-binder combinations

that gain stiffness faster will lead to shorter time delays to open the road to traffic. The decision to choose the minimum value was made on the premise that each of the field projects exhibited satisfactory performance. A particular emulsion-aggregate combination that meets the lower limit will ensure that it delivers adequate performance while minimizing traffic delays, thus justifying the concept of “optimal time” to open a newly constructed surface treatment to traffic. A marked difference was observed in the rate at which stiffness gains over time for cationic versus anionic emulsions. It has been reported in literature that cationic surfactants have a relatively lower hydrophilic character. This eventually results in faster breaking rates for cationic emulsions and a higher rate of moisture loss as compared to anionic emulsions and this might explain the differences observed in the stiffness measures for cationic and anionic emulsions. Therefore, the thresholds for the shear modulus were proposed at 2.2 kPa and 4.3 kPa for anionic and cationic emulsions, respectively.

Project Location	Material	Time to open	% Water Lost	G*
Giddings, TX	HFRS-2P + Light Weight Agg	24 hrs	79.12	2.2 kPa
Mason, TX	CRS-2P + Dolomite	4 hrs	70.19	4.3 kPa
Comanche, TX	CRS-2H + Limestone	1hrs	78.00	4.4 kPa

Table 3.3: Water Lost and Complex Shear Modulus at the time of opening to Traffic

3.6. APPLICATION

One of the primary objectives of this study was to be able to determine the optimal time to open a newly constructed surface treatment to traffic. The models presented as part of Equations 3.2 and 3.4 will help one to determine the amount of setting that the emulsion will undergo and its corresponding complex shear modulus as a function of time, weather conditions and material characteristics. Thus, the time to open to traffic will be the time interval that ensures a 75.8% reduction in the moisture and a complex shear modulus of 2.2/4.3 kPa for anionic and cationic emulsions, respectively. The equation below represents the setting model that has been presented as part of Equation 3.2 which is now being solved for the conditions stated below to back calculate the time before it can be opened to traffic.

$$75 = 100\left\{1 - e^{\left[(-0.2386 - 0.015L + 0.0365Q + 0.0291W)x^{1.0045VPD + 0.1202CMS + 0.0456HF + 0.3606CRS}\right]}\right\}$$

Considering a hypothetical scenario with an average temperature during paving of 95°F with 55% relative humidity and sustained wind speeds of 10 mph, the time to open to traffic for a chip seal application that uses a CHFRS-2P emulsion with limestone aggregates should be 5 hours.

The model presented in Equation 3.4 offers the advantage of being able to estimate the complex shear modulus of the partially cured emulsion residue. In this case for the conditions stated above, the emulsion residue offers a stiffness value of 5.5 kPa at the time when it is opened to traffic which is greater than the threshold value (4.3 kPa) warranted by the findings of this study.

However if the stiffness of the residue failed to meet the minimum required complex modulus as proposed earlier, it would have implied that the time to open to traffic is inadequate to ensure satisfactory performance of the chip seal. In a scenario like that, one would need to revise the time for opening the newly constructed chip seal to traffic so as to meet both criteria – the stiffness of the residue as well as the amount of water lost to evaporation. Failure to meet either of them can lead to early problems and subsequent failure of the surface treatment.

Chapter 4: Characterization of the Breaking and Curing Trends in Asphalt Emulsions using Electrokinetics

This chapter presents a theoretical understanding of the current flowing through a circuit when an emulsion separates into its constituent phases when placed in an electric field. The magnitude of this current depends on a set of material properties that include the emulsion's viscosity, surface potential, and dielectric of the medium and the strength of the electric field. The following section describes in detail the formulation of the mathematical equation that was developed as part of this research work, following which the proposed equation is validated with measured data. The proposed equation was further utilized in developing a methodology to determine the breaking characteristics of asphalt emulsions.

4.1. METHODOLOGY

Emulsions are defined as suspensions of two immiscible substances that are stabilized using a surface active agent. A surface active agent dissociates in the aqueous media to yield a finite concentration of ionic species that are responsible for the electrostatic forces acting between the dispersed and the continuous phases in the emulsion. Depending on the nature of the emulsion, these ionic species bind with the lipophilic or hydrophilic phase and result in mutual repulsion between the like particles and prevent them from coagulation. Thus, surface active substances (surfactants) increase the stability of emulsions so that the emulsion does not change significantly over time (McClements, 2005).

The final objective of this study focuses specifically on developing a theoretical understanding that would help quantify the breaking characteristics of asphalt emulsions by subjecting it to an electric field and subsequently recording the current v/s time signature. The proposed methodology is based on the premise that under the influence of an electric field, the ionic species in the emulsion are attracted towards the opposite polarities of an electric circuit which results in the flow of current in the cell. The magnitude of the current will depend on the strength of the electric field and properties of the electrolytic medium. The strength of the electric field is critically important as it determines the magnitude of the electric force that is experienced by a unit charge present within its perimeter (Bennet, 1974). Therefore, the higher the electric field, the faster the charged particles (or ions in this case) will travel towards the opposite polarity in the cell.

The charged particles originate from spontaneous dissociation of the surfactants in the aqueous solution. These ionic species can be assumed to be evenly distributed in the bulk fluid with a certain molar concentration depending on the formulation of the emulsion. In general, it has been pointed out that slow setting emulsions have higher concentration of surface active agents as compared to rapid setting emulsions (SFERB, 2008). In the aqueous solution, the dissolved ions are primarily responsible for transferring the charge from the cathode to the anode within the apparatus. Therefore as part of the process, the ionic species in the aqueous solution traverses through the aqueous solution as the emulsion starts to break down in the presence of an electric field. The rate at which these particles move is governed by two fundamental forces acting on the charged species: the viscous drag and a force exerted by the electric field.

Viscosity describes a fluid's internal resistance to flow and considered as a measure of fluid friction. The viscosity of the liquid medium provides a resistance that opposes the motion of these ionic species. This implies that the viscosity of the asphalt emulsion acts as the barrier to the free movement of the charged species. As the asphalt emulsion starts to break down, the charged colloidal particles will adhere to the cathode/anode depending on the nature of the emulsion. With gradual breakdown of the emulsion, it is expected that the viscosity of the emulsion will diminish and so will the viscous drag acting on the ionic species. This would lead to a net increase in the mobility of the ionic species which would imply higher ionic conductivity in the bulk fluid. On the other hand, keeping in mind that asphalt is non-polar in nature, as the emulsion breaks down and starts adhering to the electrodes, it will result in a net increase in the resistance in the circuit. This implies that the strength of the electric field will diminish as the emulsion continues to break down until it is completely insulated. Given that the electric field is the governing force that results in the flow of current through the circuit, it is understood that the process will terminate when the strength of field drops to zero. Figure 4.1 illustrates this phenomenon graphically, showing the start and end conditions of this process.

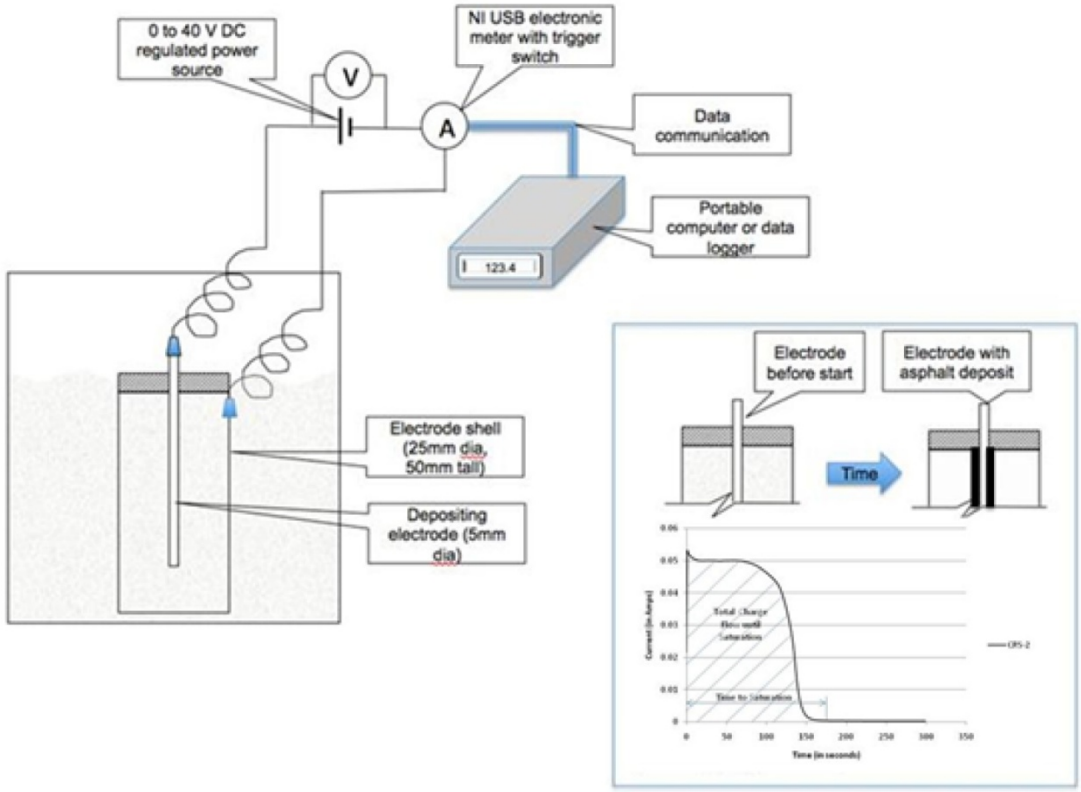


Figure 4.1: Schematic of the instrument and Initial & Terminal Conditions in the Apparatus

Another critical aspect associated with breaking of asphalt emulsions in the presence of an electric field relates to the concept of dielectric constant (Hector et al., 1936). A liquid medium can be broadly classified into two groups: polar and non-polar. The dielectric constant of the solvent provides a measure of a solvent's polarizability. The dielectric constant measures the solvent's ability to reduce the field strength of the electric field surrounding a charged particle immersed in it. This implies that the strength of the electric field will be much more pronounced for polar solvents. It is known that the dielectric constant of a particular medium is an aggregate property of the constituent

materials (Roberts et al., 2008). As previously mentioned, asphalt emulsions contain about 65% by weight of bitumen and 35% water. Asphalt is non-polar and has a dielectric of 2.6 at 20°C compared to 80.1 for that of water. The dielectric constant for asphalt emulsions is estimated at 29.7 at 20°C. However, as the emulsion starts to break down, it will result in a gradual increase in the dielectric of the fluid medium due to separation of non-polar phase (asphalt droplets) from the bulk of the fluid. This would imply that there is lesser potential for damping of the electric field. This would result in a net increase in the electric force acting on the individual charged species and their mobility.

The final aspect that is important to the understanding of this phenomenon relates to the polarity of the colloidal particles that are themselves negatively or positively charged due to adsorption of surface charges. The presence of a net charge on a particle affects the distribution of ions surrounding it, resulting in an increase in the concentration of counter-ions. The region over which this influence extends is called the electrical double layer. As the particle moves through a solution, due to the applied voltage, the ions move with it. At some distance from the particle there exists a “boundary”, beyond which the ions do not move with the particle as the surface potential drops with increasing distance. The potential that exists at this boundary is known as the zeta potential. Given this definition, it can be concluded that the higher the surface potential, the higher the electrostatic forces of attraction between the particle and the ions present within the electrical double layer. In the case where the emulsion is subjected to an electric field, this would affect the total number of available ions contributing to the ionic conductivity of the solution. Therefore, it could be expected that emulsions with higher

surface potentials will have lower number of available carriers compared to those with lower surface potential. Typically, high zeta potentials are characterizing features for stable emulsions, or slow-setting emulsions in the context of bituminous emulsions while lower zeta potentials are reported for rapid-setting emulsions (Hunter, 1986; Hunter, 1993).

In summary, the velocity of the particle depends on the following factors:

- Strength of electric field
- The dielectric constant of the medium
- The viscosity of the medium
- The zeta potential

Henry's equation combines each of these individual factors and proposes the following constitutive relationship for mobility of the charged particles in solution (Dukhin et al., 1974):

$$\mu_E = \frac{2\varepsilon\zeta f(Kr)}{3\eta} \qquad 4.1$$

Where

μ_E : Electrophoretic mobility

ε : Dielectric constant of the medium

η : Dynamic viscosity of the medium

$f(\kappa r)$: Henry's function

κ^{-1} : Debye length

r : Particle radius

Typically, Henry's function is approximated as 1.0 or 1.5, depending on the thickness of the double diffused layer. Laboratory determination of particle size distribution showed that the asphalt emulsions that were studied had mean radii in excess of 0.2 microns. This implies that the Smoluchowski's approximation ($f(\kappa r) \approx 1.5$) could be adopted for the purpose of this study (Smoluchowski, 1903).

Therefore, Equation 4.1 can be simplified as given below:

$$\mu_E = \frac{\varepsilon\zeta}{\eta} \qquad 4.2$$

In the case of low Reynolds number (laminar flow) and moderate electric field strength, the velocity of a charged particle is proportional to the field strength, which is expressed as follows:

$$\mu_E = \frac{v}{E} = \frac{vd}{V} \qquad 4.3$$

Where

v : Velocity of the charged particle

V : Potential difference

d : Distance between the two polarities

E : Electric field strength

Equations 4.2 and 4.3 could be combined to write the following generalized relationship for determination of the velocity of the charged particle:

$$v = \frac{V\varepsilon\zeta}{\eta d} \qquad 4.4$$

As explained in the foregoing discussion, the dispersed particles will start traversing through the solution and adhere to the oppositely charged electrode. Asphalt being non-polar, will act as an additional resistor whose magnitude builds with time. Furthermore, as the asphalt droplets start to deposit on the electrodes, the "effective" distance between the two electrodes will continue to reduce which will affect the strength of the electric field acting on the charged particles in the solution. Therefore, Equation 4.4 needs to be revised in order to take into account the dynamic nature of the properties of the emulsion. Thus, in time domain Equation 4.4 should be modified as given below:

$$v(t) = \frac{V(t)\varepsilon(t)\zeta}{\eta(t)d(t)} \qquad 4.5$$

Where

V(t) : Applied voltage at any instant, t

ε(t) : Dielectric constant of the medium at any instant, t

η(t) : Dynamic viscosity at any instant, t

d(t) : "Effective" distance between the two electrodes at any instant, t

Electric current is the rate of flow of electric charge through a conductive medium and can be expressed as,

$$i = \frac{\Delta Q}{\Delta t} \qquad 4.6$$

Where

ΔQ/Δt : Net flow of charge (C) in the time interval Δt

The flow of current can be associated with the bulk charge density and the mobility of the charged particles in the solution using the following relationship:

$$i = \frac{\Delta Q}{\Delta V} \times \frac{\Delta V}{\Delta t} \quad 4.7$$

Where,

$\Delta Q/\Delta V$: Bulk charge density, C/m^3

$\Delta V/\Delta t$: Flow rate, m^3/sec

Given that Equation 4.5 provides a relationship between the particle velocity and the material properties, one can determine the volumetric flow rate as a function of time using the relationship as given below:

$$\frac{\Delta Q}{\Delta t} = \pi h \left\{ \left(R + \frac{V}{d} \cdot \frac{\varepsilon \zeta}{\eta} \right)^2 - R^2 \right\} \quad 4.8$$

Where,

R : Radius of the apparatus, m

Equation 4.8 applies to cylindrical geometry of the electrodes. However, as the emulsion starts to break down into its constituent phases, the properties of the emulsion will start to evolve and therefore Equation 4.8 can be modified as given below to reflect the changes occurring in time scale:

$$\frac{\Delta Q}{\Delta t} = \left(\pi \left(\left(R(t) + \frac{V(t)}{d(t)} \cdot \frac{\varepsilon(t) \zeta}{\eta(t)} \right)^2 - R(t)^2 \right) h \right) \quad 4.9$$

Equations 4.6 and 4.9 can be combined to develop a constitutive relationship for the current flowing through the apparatus (see Equation 4.10).

$$i(t) = \frac{\Delta Q}{\Delta V} \cdot \pi h \left\{ \left(R(t) + \frac{V(t)}{d(t)} \cdot \frac{\varepsilon(t)\zeta}{\eta(t)} \right)^2 - R(t)^2 \right\} \quad 4.10$$

4.2. RESULTS

Equation 4.10 provides a constitutive relationship between the net current flowing through the emulsion sample and the measurable parameters for a given emulsion sample. The following paragraphs discusses in detail the methodology adopted in the determination of each of these individual parameters.

The validation of the aforementioned theory was undertaken for five different scenarios that helped the author understand the effect of different material properties on the flow of current. The study included two different emulsion samples: CRS-2 and CRS-2P, of which the latter was diluted at 10, 20 and 30% to study the effect of dilution ratios on the current flowing through the circuit.

4.2.1. Determination of Charge Density of the Emulsion Samples

In an electric field, the dissolved ions act as carriers of charge and contribute to the flow of current. Therefore, in order to determine the current flowing through the circuit theoretically, it is essential to determine the density of the ionic species in the solution. Inductively coupled plasma optical emission spectrometry (ICP-OES) uses an inductively coupled plasma to produce excited atoms and ions that emit electromagnetic radiation at wavelengths characteristic of a particular element (Stefansson et al., 2007). The intensity of this emission is indicative of the concentration of the element within the sample. This

technique was utilized for determining the ionic concentration in the emulsion samples. Table 4.1 summarizes the bulk charge densities that were measured for the emulsion samples considered.

Type of Emulsion	Dilution Ratio	Chloride Concentration (M/l) [Mean]	Coefficient of Variation (%)
CRS-2	N/A	0.07	0.11
CRS-2P	N/A	0.27	0.03
	10%	0.24*	
	20%	0.22*	
	30%	0.19*	

Table 4.1: Measurements Obtained for the Bulk Charge Density using ICP-OES

* Denotes that the reported ionic concentration was calculated using the ionic concentration of the CRS-2P sample and the dilution ratio that was used for preparation of the specific sample.

4.2.2. Determination of Viscosity of the Emulsion Samples

The viscosity of the emulsion in the laboratory was determined using Shell cups as it provides an easy and reliable tool for measurement of viscosity for a wide range of fluids at different temperature, pressure and flow rates. The viscosity measurements for each of the five samples are summarized in Table 4.2.

Type of Emulsion	Dilution Ratio	Viscosity (Pa-sec) [Mean]	Coefficient of Variation (%)
CRS-2	N/A	4.31	3.6
CRS-2P	N/A	3.38	4.5
	10%	3.33	3.8
	20%	3.29	6.2
	30%	3.26	5.3

Table 4.2: Measurements Obtained for the Viscosity of the Emulsion Samples

As the emulsion starts to break down, its physical properties evolve because the charged colloid particles deposit on the oppositely charged electrode. In the context of viscosity measurements, it would imply that the viscosity of the bulk fluid drops as the viscous phase (asphalt) is filtered out of the solution. The author assumed that the resulting change in viscosity is linearly proportional to the amount of asphalt that is separated from the bulk solution.

4.2.3. Determination of the Dielectric Constant of the Emulsion Samples

It is assumed that the dielectric of the emulsion sample is equivalent to the weighted average of the dielectric of asphalt and water. Table 4.3 summarizes the dielectric constant for each of the individual emulsion samples that were used in this study at the start of the experiment.

Type of Emulsion	Dilution Ratio	Relative Permittivity
CRS-2	N/A	29.9
CRS-2P	N/A	29.9
	10%	34.9
	20%	39.9
	30%	44.9

Table 4.3: Relative Permittivity of the Emulsion Samples

As with other properties, the dielectric of the emulsion evolves as the material starts to break down. The gradual separation of the dispersed phase (asphalt) from the emulsion will result in a lower relative proportion of asphalt particles in the solution causing the dielectric of the overall solution to increase with time: less asphalt and more water available. This implies that the solution will serve as a better conducting medium and contribute to higher mobility for the charged particles in the solution.

4.2.4. Determination of the Surface Potential of the Emulsion Samples

Equation 4.10 indicates that the mobility of the ions in the solution depend on the surface potential of the dispersed phase, also referred to as the ζ-potential. The determination of the ζ-potential for the asphalt emulsions was undertaken using a diluted solution of the emulsion sample. The reported ζ-potential values were determined using dynamic light scattering measurements performed on the diluted samples. The principle behind such measurement involves movement of the charged particle through an interference pattern that results from the intersection of two coherent beams of light. The ionic mobility was

determined after analyzing the interference pattern as the charged particle scatters light only in the bright regions and not in the dark regions (Hunter, 1993; Horne, 1995). Table 4.4 summarizes the ζ-potential measurements performed on the two emulsion samples.

Type of Emulsion	ζ-potential (mV)	Coefficient of Variation (%)
CRS-2	37.3 (pH = 12.2)	2.1
CRS-2P	48.1 (pH = 11.7)	3.6

Table 4.4: ζ-Potential Measurements Conducted on the Emulsion Samples

4.2.5. Determination of Electric Field and Resistivity of the Emulsion Sample

The gradual separation between the continuous and dispersed phases of the emulsion and the subsequent deposition of the asphalt droplets on the electrode increases the net resistance in the circuit. This implies that the actual voltage between the two electrodes will recursively diminish with time until one of the electrodes is practically insulated. This also suggests that the strength of the electric field will get weaker with time which will lower the ionic mobility. Therefore in order to determine the voltage drop across the circuit, it is important to determine the resistivity of the emulsion samples included in this study. Most bench-top instruments are designed to measure the conductivity of any given material, which is the inverse of the resistivity of the given material. The author measured the conductivity of the sample specimens using one such instrument that uses a pair of coaxial cylinders. The two electrodes are positioned by dielectric separators that never contact the liquid under investigation. The electrodes are immersed in the liquid to a specified depth and the electrical conductivity is calculated from the change in measured

conductance. The measured conductivities for the aforementioned samples are summarized in Table 4.5.

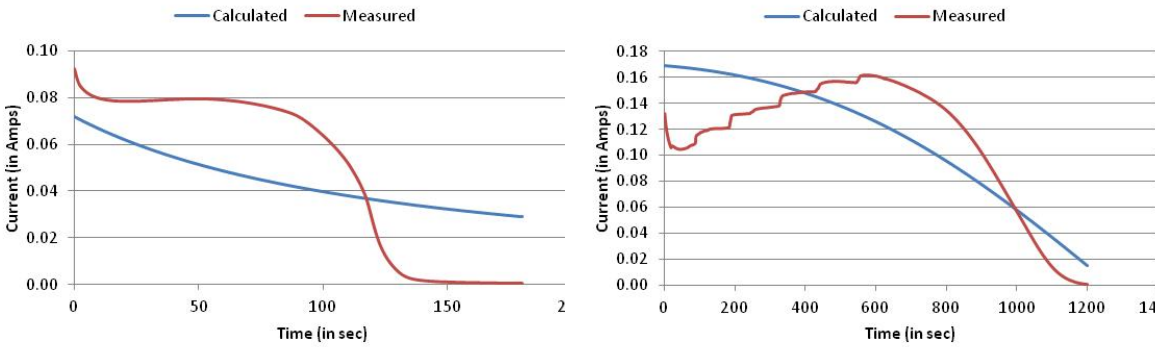
Type of Emulsion	Dilution Ratio	Conductivity (S/m)
CRS-2	N/A	2.22
CRS-2P	N/A	6.90
	10%	8.93
	20%	13.26
	30%	14.11

Table 4.5: Conductivity Measurements Conducted on the Emulsion Samples

4.2.6. Theoretical versus Measured Current Flow

4.2.6.1. Influence of Emulsion Type

Figure 4.2 shows the theoretical and measured current flow for the two emulsion samples used in this study – CRS-2 and CRS-2P.



CRS-2 CRS-2P

Figure 4.2: Calculated V/s Measured Current for the Emulsion Samples

The results presented in Figure 4.2 demonstrate that the calculated and measured flow of current follow the same general trend in either of the emulsion samples. In the case of the CRS-2 emulsion sample, it can be observed that although the measured value reaches zero after 150 seconds from the time the circuit is switched on, the theoretically calculated values suggest that it reaches an asymptotic value around 0.02 Amps after 180 seconds. However, it is interesting to note that the measured and the calculated peak current flows are in agreement. On the other hand, for the CRS-2P emulsion sample, the results presented in Figure 4.2 suggest that that the calculated and measured current flows though initially different, closely resemble each other at later stages of the experiment. It was observed that both each of the two datasets requires approximately 20 minutes until the circuit is completely insulated. Noteworthy of mention, the measured value showed an upward followed by downward trend in the current flow which was not observed in the calculated values. The particular finding could be attributed to pH changes that can result from secondary electrochemical reactions which will eventually affect the ζ-potential and ultimately alter the mobility of the ions.

4.2.6.2. Influence of Dilution Ratio

Figure 4.3 shows the theoretical and measured current flow for the CRS-2P emulsion sample at three different dilution ratios – 10%, 20%, and 30%. A dilution ratio of 10% implies that the emulsion was diluted to 9 parts by weight of the emulsion and 1 part by weight of water.

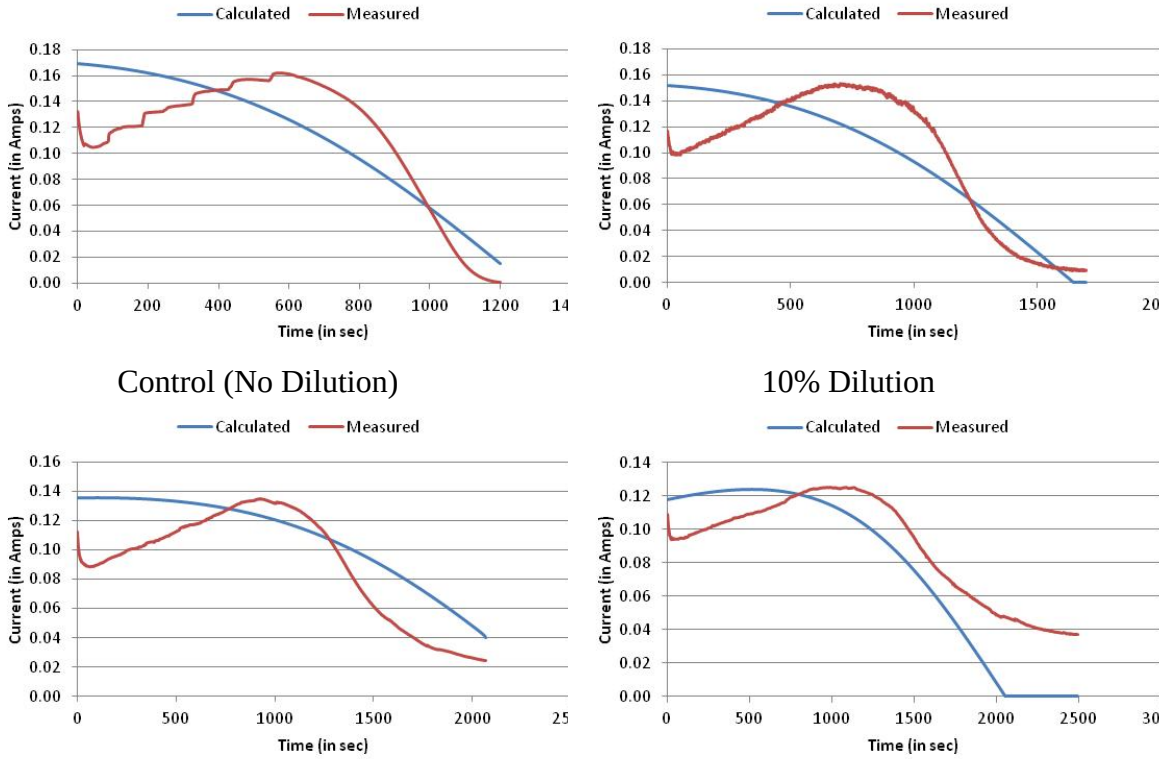


Figure 4.3: Calculated V/s Measured Current for the CRS-2P Sample at Different Dilution Ratios

The results presented in Figure 4.3 show that the calculated and measured current flows for the CRS-2P emulsion sample resemble each other closely. Although there are apparent differences in between the two datasets at initial stages of the experiment, the time to reach their asymptotic values are almost the same for each of the three dilution ratios used in this study. Furthermore, it can be also seen that the initial current value for either of the two datasets have noticeable resemblance and there is a gradual decrease in their values for increasing ratios of dilution for either of the datasets.

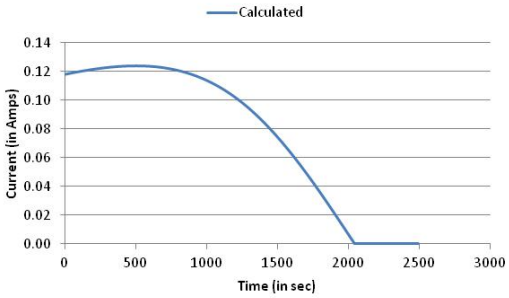
4.2.6.3. Parametric Analysis

The objective of this exercise was to study the sensitivity of the current-time signature to variations in material properties. The author selected four different input parameters based on preliminary trials which are as given below:

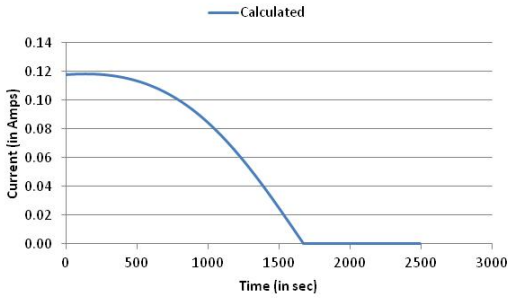
- Resistivity
- Ionic Concentration
- Mobility
- Dielectric Constant (Relative Permittivity, ε)

Of the four input parameters, although resistivity does not physically appear in the constitutive equation proposed earlier, it still plays a significant role as it determines the drop in the strength of the electric field as the emulsion starts to separate into its constituent phases. Figure 4.4 demonstrates graphically the results of the parametric analysis that was undertaken. In the control experiment, the chosen values for these four inputs were as given below:

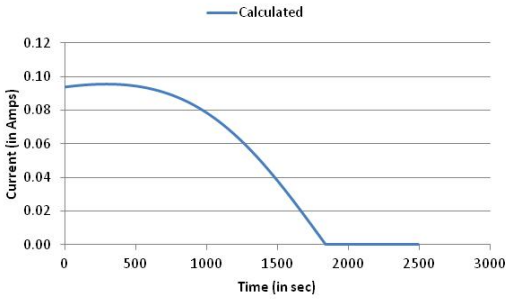
- Resistivity (ρ) : 0.10 Ω-m
- Ionic Concentration (I) : 0.2 M/l
- Mobility (μ_e) : 3×10^{-8} m^2/V
- Relative Permittivity (ε) : 35



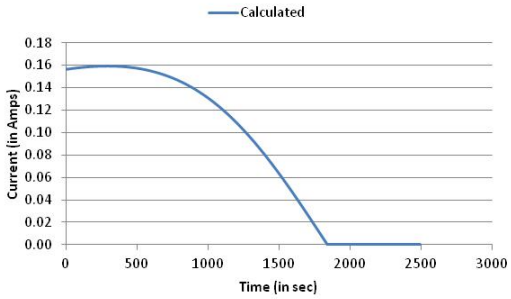
$\rho = 0.09\ \Omega\text{-m}$



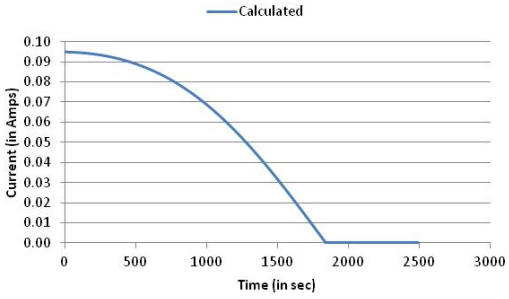
$\rho = 0.11\ \Omega\text{-m}$



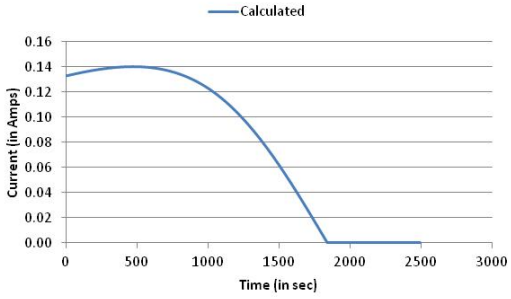
I = 0.15 M/l



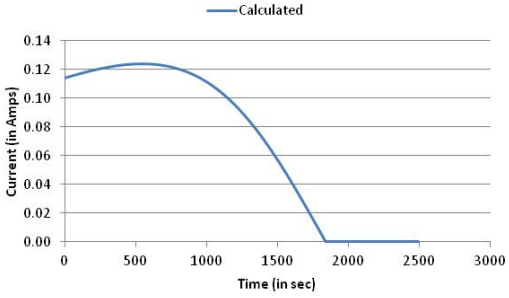
I = 0.25 M/l



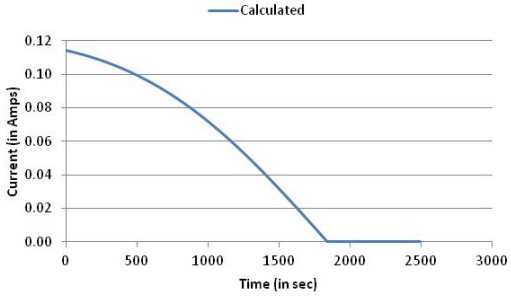
$\mu_e = 2.5\times10^{-8}\ m^2/V$



$\mu_e = 3.5\times10^{-8}\ m^2/V$



$\varepsilon = 25$



$\varepsilon = 42$

Figure 4.4: Parametric Analysis of the Proposed Equation to Study the Sensitivity of the Equation to Material Properties

Figure 4.4 demonstrates that depending on the value of a set of input parameters, there is a marked difference in the current-time signature of a given material, provided all other properties are held constant. It was interesting to note that, for certain combinations of the input parameters, one can observe a non-monotonic signature as opposed to others where it is a steadily decreasing function. Therefore, it is evident that subtle differences in material properties can translate into significantly different current-time signature of the material.

4.2.6.4. Discussion

The results presented above indicate that the theoretical formulation of the problem explains the fundamental principles associated with breaking of an emulsion into its constituent phases in an electric field. However, the author realized that there are secondary effects that are not addressed in the current formulation of the problem. The most prominent of these being the effect of pH changes on the ζ-potential of the emulsion which will affect the mobility of the ions. However, given these limitations, the proposed equation still provides a reasonable insight into the dynamics of the process and how different material properties affect the flow of current and hence the breaking of the emulsion.

From a practical standpoint, the aforementioned formulation could be used for studying the breaking characteristics of different asphalt emulsions, provided one can obtain the necessary material properties that include the ζ-potential, resistivity of the asphalt binder, dielectric of the medium, and viscosity of the emulsion.

4.3. Development of a Test Procedure based on the Proposed Equation

4.3.1. Working Principle

Several studies in the past have used electrokinetics and basic material properties to better understand the stability of asphalt emulsions and the ability of asphalt emulsions and binders to adhere to aggregate surfaces. For example, Poirier et al. (1989) measured the zeta potential of asphalt droplets in dilute conditions using electrokinetic techniques and compared the results to adsorption isotherms of emulsions on different solid surfaces. Labib (1992) used zeta potential of asphalt binders and aggregates to identify their ability to adhere with each other. Liu et al. (2002) measured the distribution of zeta potential of bitumen and clays to predict their interaction in an aqueous solution. In fact, an electrokinetic method is also commonly used to distinguish between a cationic and an anionic emulsion. However, in this study the author attempted to quantify the breaking rate of emulsions, driven by its material properties such as ion concentration and zeta potential, in real time by recording the current flow through the emulsion.

The methodology used in this study consisted in applying a direct current (DC) potential across a sample of an asphalt emulsion and record the current passing through the emulsion in real time (Figure 4.5). The current flowing through the emulsion is dictated by the collective electric force acting on the ions and colloid particles in the emulsion as well as the viscous drag experienced by these ions and the colloid particles as they start to drift towards the oppositely charged electrodes. The two forces, electric force and viscous drag, are opposite in nature as the viscous drag opposes the mobility of the charged particles in the solution. As shown in Equation 4.10, at any instant the

current or the rate with which the charged asphalt droplets (or ions) move towards the oppositely charged electrode is a function of the dielectric constant of the medium, the zeta potential, the dynamic viscosity of the emulsion and the strength of the electric field acting across the emulsion (Dukhin et al., 1974). It should be noted in this context that the dynamic viscosity is a function of temperature. In order to avoid any secondary interference due to fluctuations in viscosity, all the experiments were conducted at 24°C.

The asphalt droplets in an emulsion are stabilized through electrostatic forces of repulsion. When subjected to an electric field, the droplets migrate towards the electrode of an opposite polarity. Migration of the asphalt droplets partially breaks the emulsion and results in the deposition of the asphalt droplets on the electrode. This in turn reduces the potential across the emulsion sample due to the poor electrical conductivity of the asphalt binder. The kinetics of the process continues (at a varying rate) until (i) the emulsion is completely broken or (ii) the amount of asphalt deposited on the electrode is adequate to insulate it, resulting in a zero potential across the partially broken emulsion sample. For typical rapid setting emulsions used in this study, the test was designed such that the latter condition was reached first (electrode was insulated with asphalt binder). For brevity, this condition is referred to as *saturation of the probe* in the remainder of this dissertation. The asphalt droplets migrate and saturate the cathode for a cationic emulsion and anode for an anionic emulsion.

In summary, the time to reach saturation depends on the material properties that govern the mobility of the dispersed particles (e.g. viscosity, dielectric and zeta potential) and extraneous factors (e.g. applied potential and geometry of the electrodes). The time

integral of the current flowing across the emulsion sample between two electrodes provides a measure of the net amount of charge that flows from the cathode to the anode to achieve saturation. The two different parameters of interest here include:

- *total charge flow until saturation* defined as the area under the current versus time curve, and
- *saturation time* defined as the time to reach saturation of the electrode.

These parameters can be used to distinguish between different types of emulsions. The most straightforward application of this test is to discriminate between cationic and anionic emulsions. This is because the migration of the dispersed particles is opposite for the two scenarios. The total saturation time can be used to differentiate between rapid, medium and slow setting emulsions. This is because the time to saturate the electrode varies considerably from one emulsion to the other. Slow setting emulsions are designed to break slower as the forces of electrostatic repulsion are relatively stronger and require a higher energy to destabilize the emulsion, which results in a longer saturation time. In addition, the time integral of the measured current or total charge flow until saturation will be much higher than that of a rapid setting emulsion due to the longer duration of the breaking process.

More importantly, the proposed test method and concomitant parameters can be used to assess whether or not the properties of a given emulsion, such as viscosity, dielectric and zeta potential have changed over time due to factors such as premature breaking or mechanical agitation. It is noted that, although this methodology does not directly measure fundamental properties of the material, it does measure the response of

the material to an external electric field that is governed by its inherent properties such as viscosity and zeta potential. The benefits of this test are its simplicity and the ability to provide a cumulative quantity that is related to the physio-chemical or physical characteristics of the emulsion.

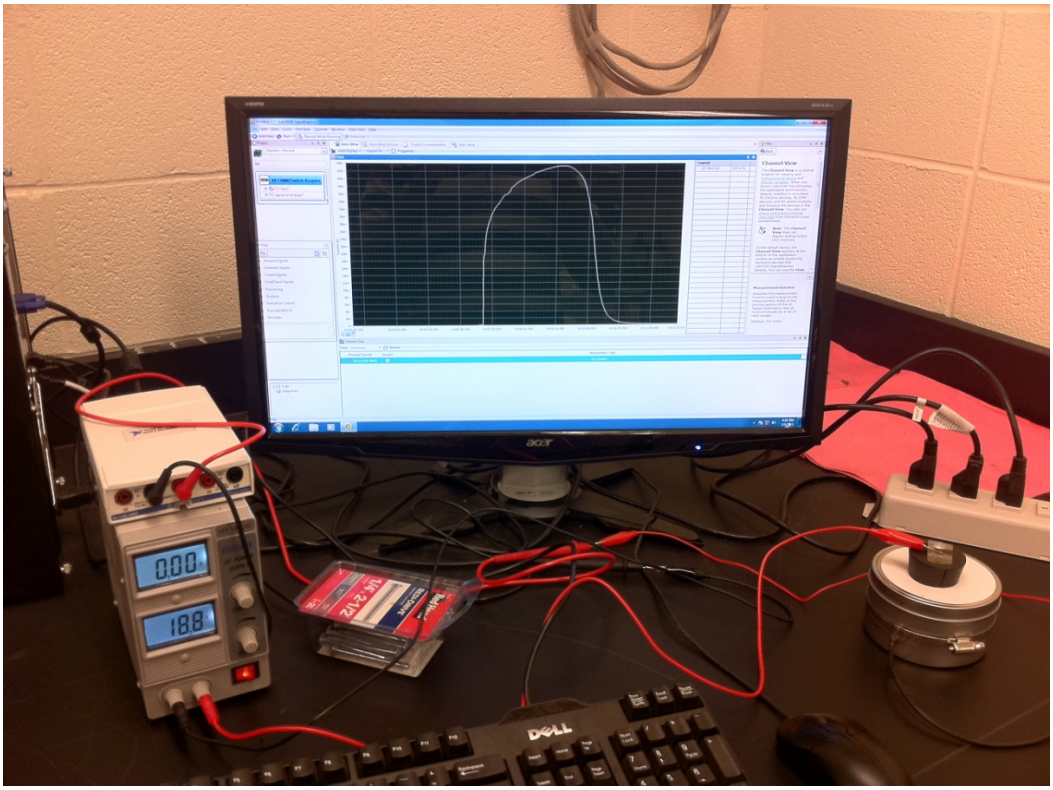


Figure 4.5: Prototype of the Instrument being used in the Laboratory

4.3.2. Test Plan and Materials

The focus of this exercise was to evaluate the sensitivity of the proposed test method and the concomitant parameters to (i) the type of emulsion and (ii) changes in a given type of emulsion (e.g. change in water content or partial breaking). These factors influence the following material properties, which in turn affect the current flowing through a sample of the emulsion:

- viscosity of the material,
- bulk ion concentration, and
- dielectric of the material

In addition, a limited number of tests were also conducted to evaluate the influence of external factors on the test method, e.g., magnitude of electric potential and geometry of the conducting probe. The following subsections describe the selection and modification of materials to achieve the objectives of this exercise.

4.3.2.1. Influence of Emulsion Type

The results presented in this dissertation show how the test parameters change for two commonly used emulsion types – CRS-2 and CRS-2P from two different suppliers. The CRS-1P emulsion was also used in this study for a limited number of tests to evaluate the overall repeatability of the test.

4.3.2.2. Influence of Dilution

The formulation of an asphalt emulsion is proprietary to the manufacturer. However, by further diluting the emulsion one can vary some of the variables associated with the rate with which the emulsion breaks. First, the addition of water to an emulsion reduces its viscosity. Second, changing the relative percentage of water and asphalt in the formulation will proportionally change the bulk ion concentration. Third, the dielectric constant of the emulsion changes since it is the weighted average of the dielectric constant of the asphalt binder and water.

4.3.2.3. Influence of Mechanical Agitation on the Properties for a Given Type of Emulsion

Physical and chemical factors govern the stability and breaking rate of an emulsion. Mechanical rolling, for example, decreases the inter-particle distance between the dispersed particles in the emulsion, thus, promoting the breaking of the emulsion (Hanz et al., 2008; Hanz et al., 2009). There is anecdotal evidence as well as published literature that confirm that emulsions can partially break during transport (Asphalt Institute, 2008). Such accidental breakage of the emulsion is typically attributed to the inherent formulation of the emulsion or to mechanical agitation during transport. One of the goals of the proposed test was to investigate whether or not it could be used to identify any accidental breaking in asphalt emulsions during transport. The mechanical shock and disturbance during transport was simulated in the laboratory through vigorous shaking in a sieve shaker for a specified duration of time.

4.3.2.4. Influence of External Factors – Geometry & Potential

The test uses electrokinetic principles to compute an index that is analogous to the energy required to break the emulsion. The test uses a circular cathode placed concentrically within an anode for a cationic emulsion. The electrodes apply the required potential that facilitates breaking of the emulsion. Thus, the results from the test are geometry dependent as the surface area available for the asphalt droplets to break and deposit will depend on the configuration and dimensions of the electrodes.

The potential difference applied across the emulsion sample affects the mobility of the ions and, therefore, the rate with which ions migrate towards the electrode of opposite polarity in the apparatus (Equation 4.10). The following factors were considered

in the test matrix to validate the influence of these external factors on the measured parameters:

- the surface area of the electrode for asphalt deposition was increased, and
- the applied potential was varied on the rate of breaking of the asphalt emulsion

4.3.2.5. Summary of Tests and Materials

The full factorial would include 96 tests without replicates. However, external factors, such as, applied voltage and the effect of surface area are important to validate the theoretical rationale for the test method. Since the objective of this study was to evaluate the feasibility of using this approach to differentiate between different types of emulsions and changes within a given type of emulsion, the three variables, type of emulsion, dilution and the effect of mechanical agitation, were of greater interest. Therefore, this study was limited to a partial factorial experiment that included these factors. It should be noted in this context that the test configuration with 18.6 V and the surface of the apparatus acting as the cathode without any dilution or mechanical disturbance was considered as the control experiment for the given emulsion and supplier. In addition, a few tests were also conducted to evaluate the influence of extraneous factors such as applied potential and surface area of the electrode. Table 4.6 presents a summary of the different materials and test configurations that were used in this study.

Factor	Source	Type	Test Configuration
Type of Emulsion	Supplier-A	CRS-2	18.6 V
		CRS-2P	
		CRS-1P	
	Supplier-B	CRS-2	
		CRS-2P	
Dilution	Supplier-A	CRS-2P	18.6 V, 10% Dilution
			18.6 V, 20% Dilution
			18.6 V, 30% Dilution
	Supplier-B	CRS-2P	18.6 V, 10% Dilution
			18.6 V, 20% Dilution
			18.6 V, 30% Dilution
Mechanical Agitation	Supplier-A	CRS-2	18.6 V, 2 hrs Agitation
			18.6 V, 5 hrs Agitation
	Supplier-B	CRS-2	18.6 V, 2 hrs Agitation
			18.6 V, 5 hrs Agitation
Effect of Geometry	Supplier-A	CRS-2	Reduced Surface Area
Effect of Applied PD	Supplier-B	CRS-1P	18.6 V
		CRS-1P	9.5 V

Table 4.6: Summary of Tests Performed

4.3.3. Test Results

4.3.3.1. Influence of Emulsion Type

Figure 4.6 shows the typical results for replicate samples of three different emulsions – CRS-2 and CRS-1P from Supplier A and CRS-2P from Supplier B.

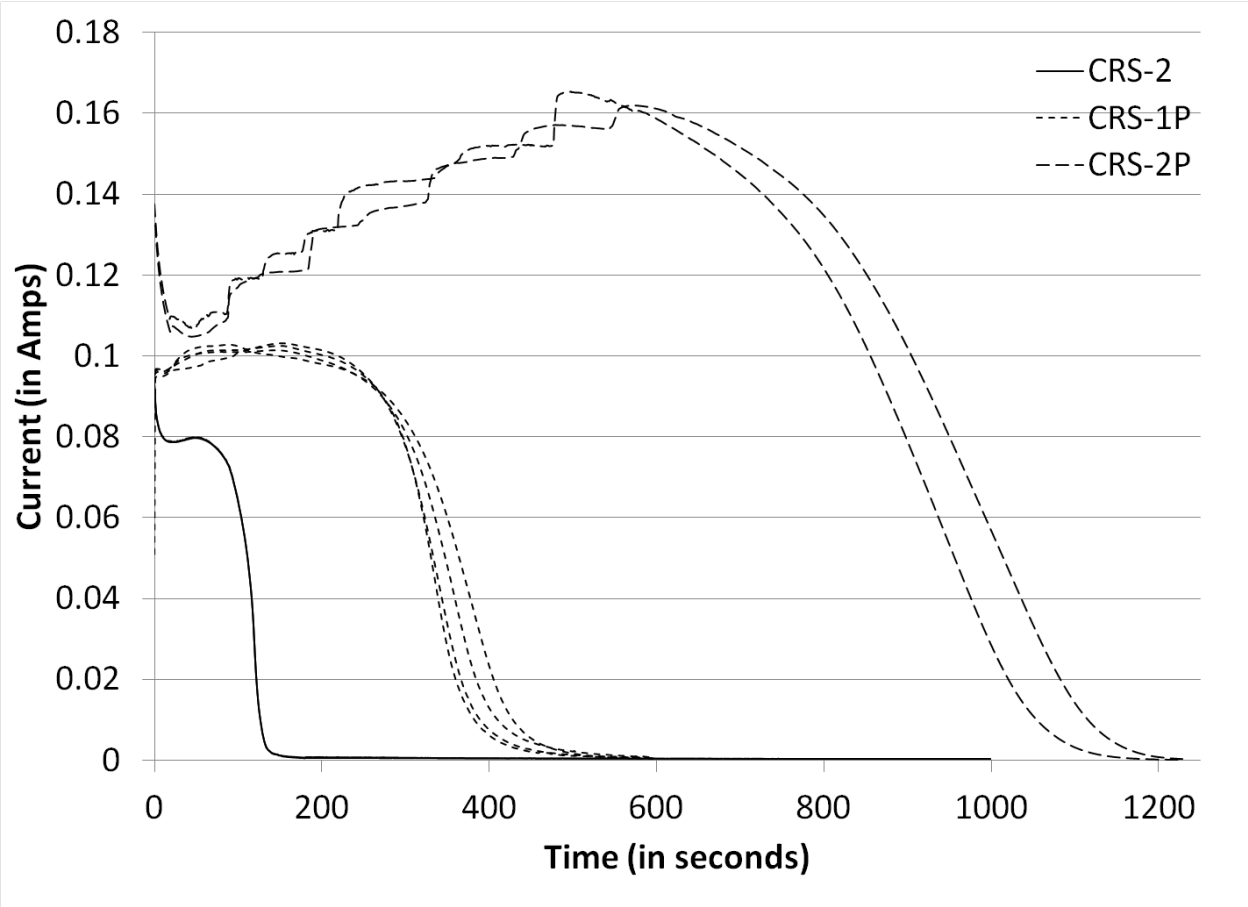


Figure 4.6: Current flow through the apparatus for a CRS-2, CRS-1P and CRS-2P emulsion with an applied voltage of 18.6V

It can be observed from Figure 4.6 that the current measurements are significantly different for the different kinds of emulsions while the current as well as the saturation

time for different replicates of a given type of emulsion closely follow each other. The saturation time and the total charge flow until saturation follow a gradual upward trend for the three emulsions: CRS-2, CRS-1P and CRS-2P in that order. Figure 4.7 illustrates the total charge flow until saturation, computed as the area under the current versus time curve. The data presented in Figure 4.7 illustrates that the total charge flow was different for each of the three emulsions.

The total charge flow is analogous to the net energy consumed in breaking the emulsion and depositing binder to saturate the electrode. This parameter can be considered as an indicator of the relative stability of these emulsion samples. The proposed methodology is able to clearly distinguish between the materials with good repeatability.

It appears from the results presented in Figure 4.6 that the resistance in the circuit drops over time just after the test is started for certain materials. It should be noted that the increase in the current flow is caused by the reduction in the viscous drag that is achieved through segregation of the asphalt droplets resulting in a net increase in the particle velocity.

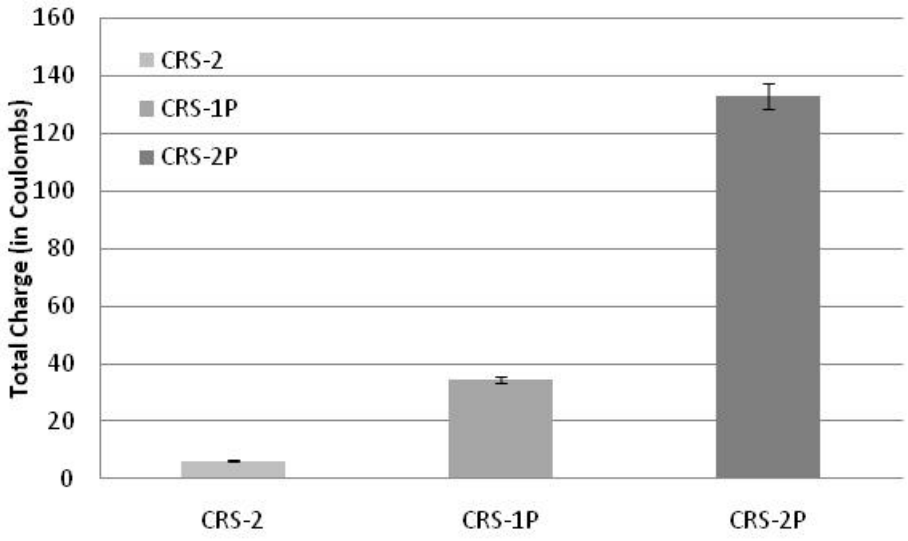


Figure 4.7: Total charge flow till saturation for CRS-2, CRS-1P and CRS-2P asphalt emulsion samples with 18.6V potential difference acting between the electrodes

4.3.3.2. Influence of Dilution for a given Type of Emulsion

Figure 4.8 illustrates that the proposed methodology is able to identify changes due to dilution. It must be noted that these tests were conducted by further diluting an emulsion sample. The author considered testing the emulsion by reducing the water content in the emulsion sample. However, this required heating the emulsion sample, which in turn resulted in non-homogenous breaking of the emulsion and formation of a "skin" on the surface. While such samples can be homogenized and tested, these were not included in this feasibility study.

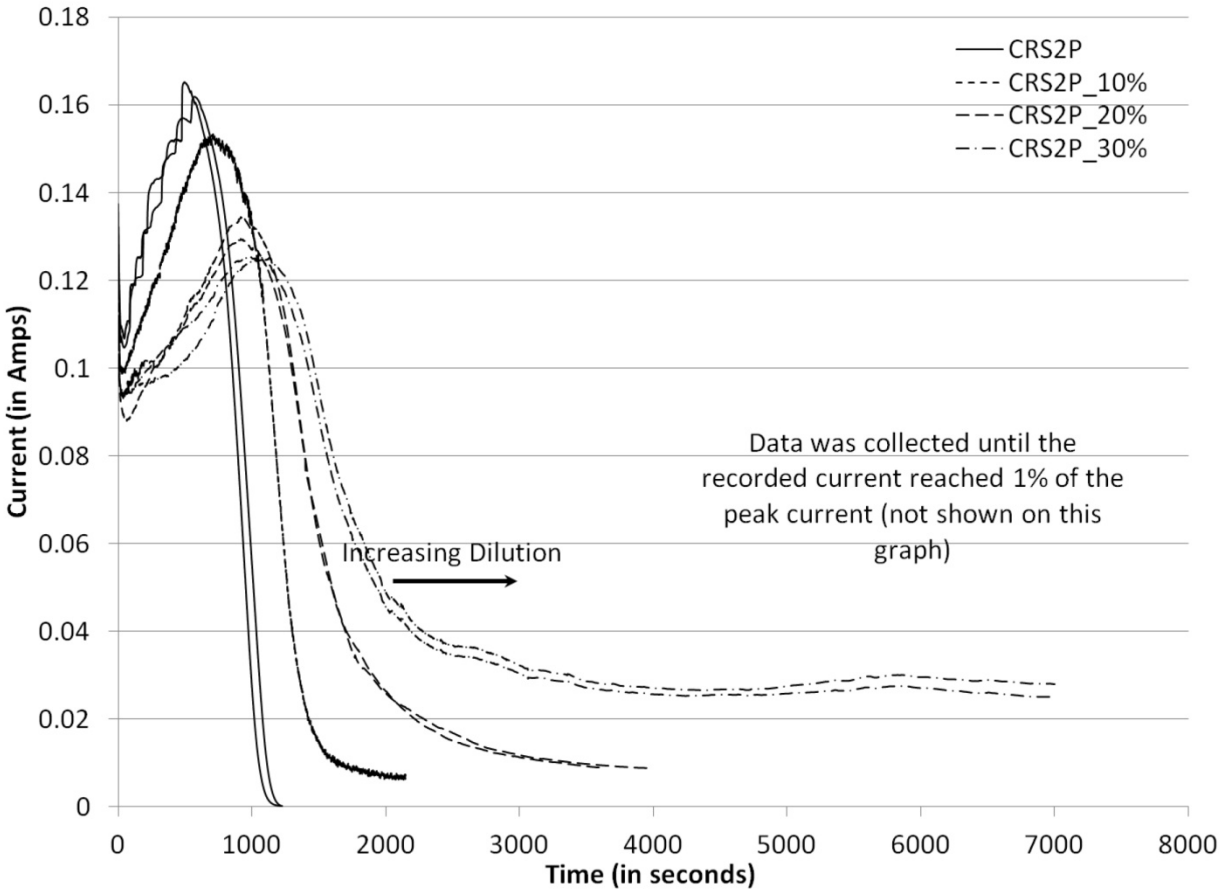


Figure 4.8: Net current flowing through the apparatus with an applied voltage of 18.6V at different dilution ratios for a CRS-2P emulsion

There is a significant shift in the measured current when the emulsion was diluted with water. The addition of water brings about changes in the dielectric and the viscosity of the emulsion. As described in the previous section, when subjected to an electric potential the emulsion breaks and deposits on the cathode (for a cationic emulsion) partially insulating it and reducing the potential acting across the remaining sample. The process continues until the cathode is saturated, i.e. asphalt binder is deposited, insulates

the cathode and stops the breaking process. Thus, the conditions in the apparatus as well as the properties of the material evolve as the process continues.

The reduction in viscosity and the increase in the dielectric of the material, due to dilution, will both translate into higher mobility. However, the decrease in the bulk ion concentration reduces the number of carriers available to transport the charge from the cathode to the anode per unit volume of the sample. Although each of these factors influences the measured current differently, the author believes that the increased mobility and the reduction in the ion concentration are the dominating factors. The theory presented can be used to calculate the response of the material under any test configuration.

Figure 4.9 illustrates the total charge flow until saturation for the different dilution ratios that were used in this study. The data presented in Figure 4.9 illustrates that the total charge flow was significantly different for the different dilution ratios, supporting the proposed theory.

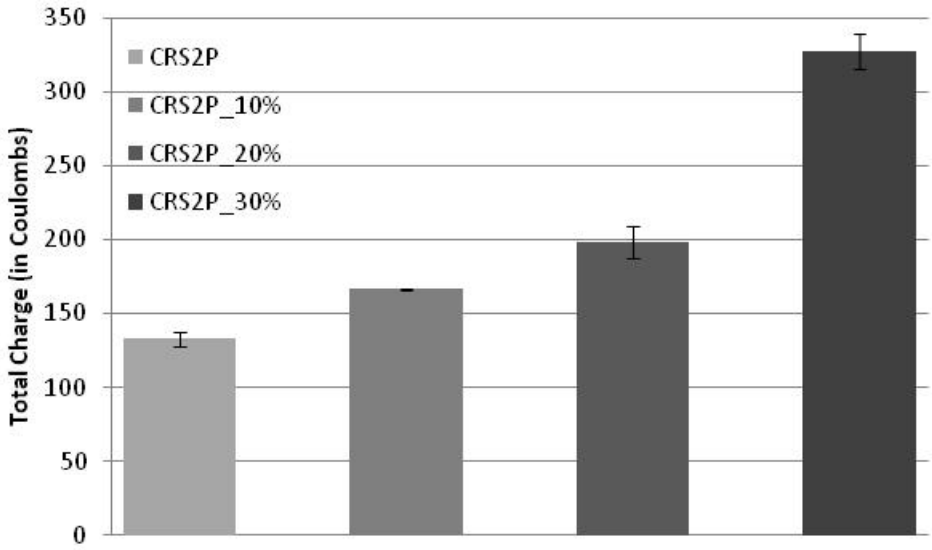


Figure 4.9: Total charge flow till saturation for CRS-2P asphalt emulsion samples @ 10%, 20% and 30% dilution

4.3.3.3. Influence of Mechanical Agitation on the Properties for a Given Type of Emulsion

In the laboratory, mechanical agitation was simulated by placing 850 grams of the material in the sieve shaker for 2 and 5 hours. The results in Figure 4.10 illustrate that mechanical agitation altered the material significantly and the test results are sensitive to such changes in the material.

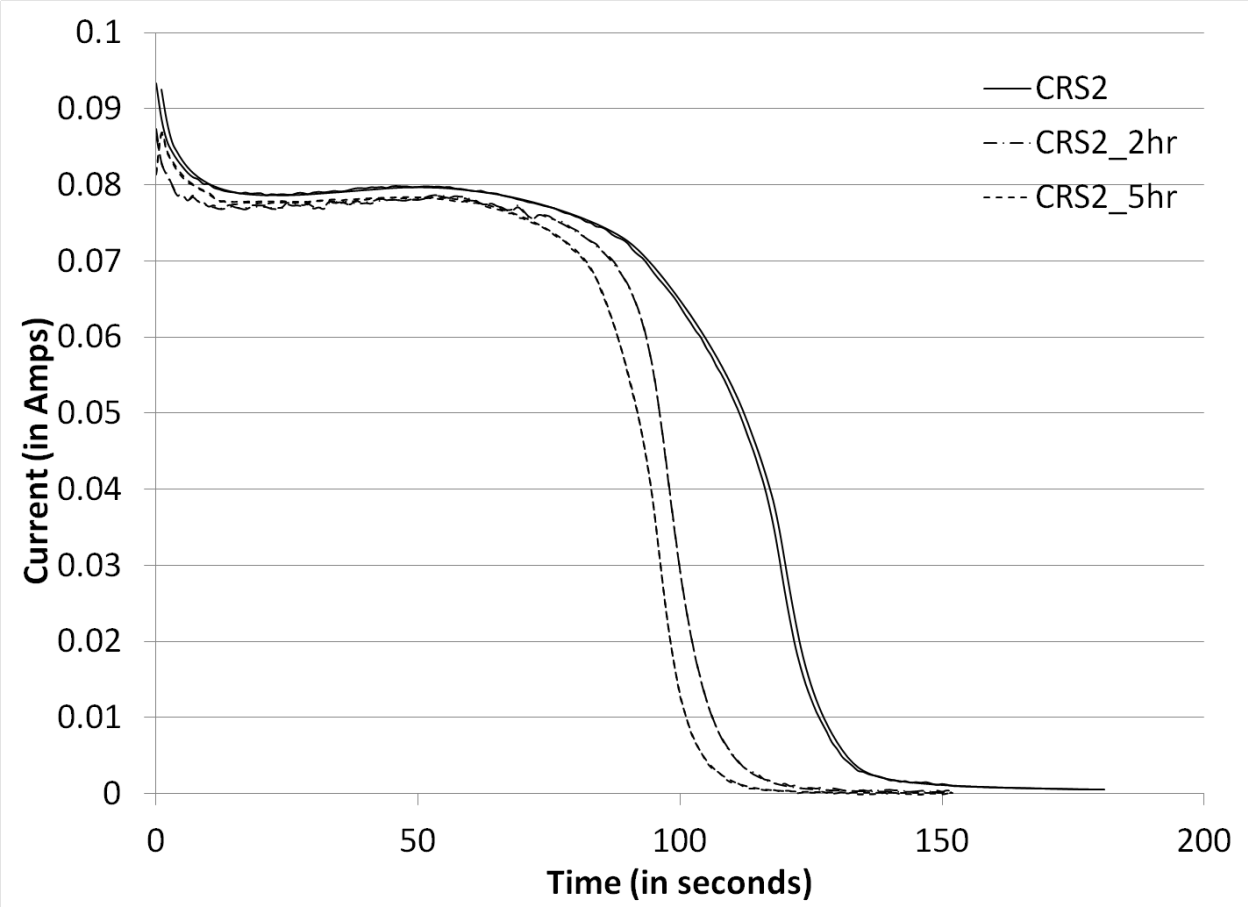


Figure 4.10: Net current flowing through the apparatus at different levels of mechanical agitation for CRS-2 emulsion sample

It is interesting to note that most of the changes in the emulsion occurred during the first two hours of agitation or less. The control samples had already experienced some level of agitation when these were transported from the producer to the laboratory via a commercial ground shipping service. Therefore, it is difficult to definitively comment on the relationship between stability and partial breaking of the emulsion due to mechanical agitation as a function of time. Nevertheless, the results clearly show that the test method is sensitive to these effects and that the effects are significant.

Figure 4.11 compares the total charge flow until saturation for each of the test configuration, i.e., the CRS-2 sample without shaking and that after 2 and 5 hours of shaking on the sieve shaker. The results indicate that the total charge flowing through the apparatus before reaching saturation diminishes as the material is exposed to a higher degree of saturation. As previously mentioned, the parameter – "total charge flow until saturation" is analogous to the energy consumed in breaking the material. The test results are consistent with the expectation that a material that has already started to flocculate under the action of mechanical agitation will require less energy to break.

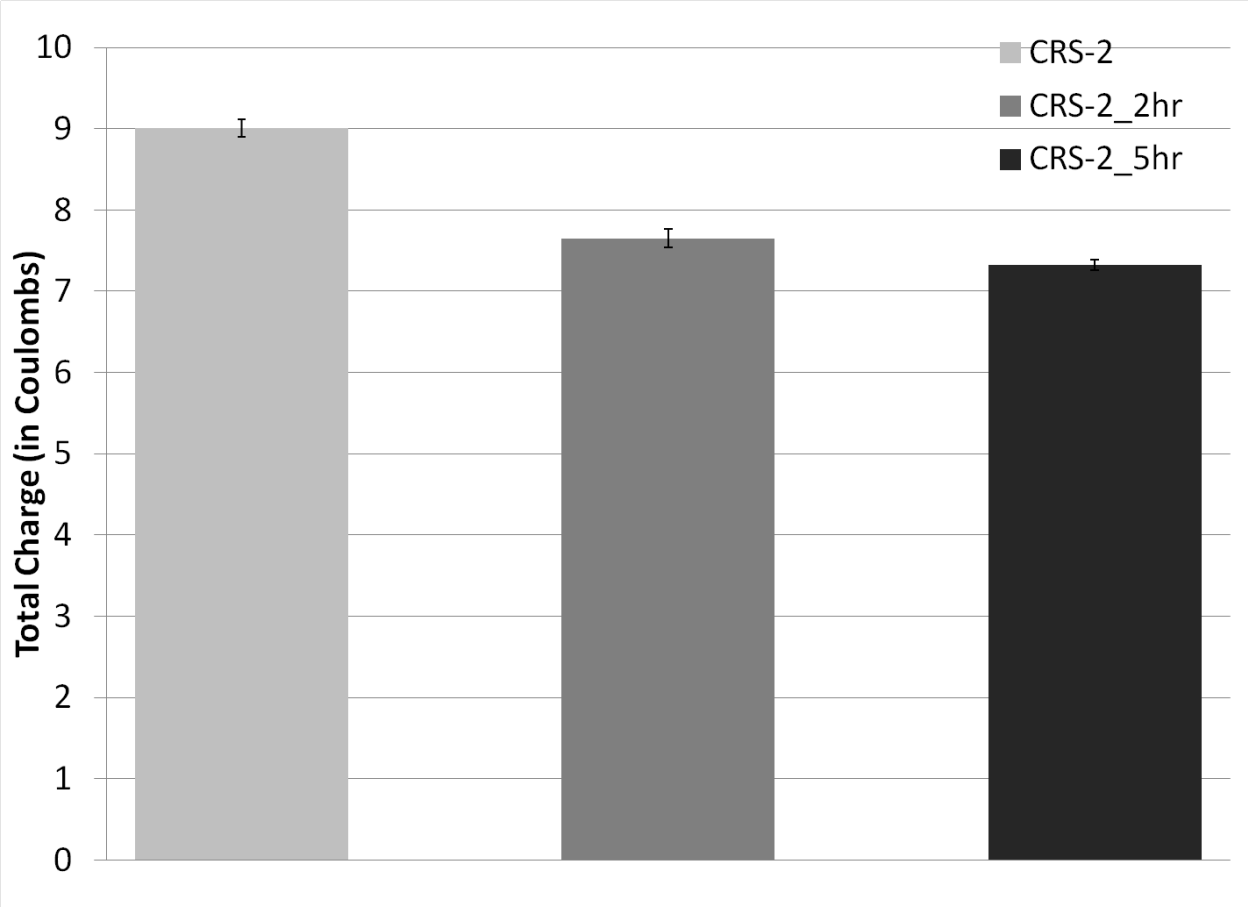


Figure 4.11: Total charge flow till saturation for CRS-2 asphalt emulsion samples after shaking for 2 and 5 hours on the sieve shaker

4.3.3.4. Influence of External Factors – Geometry & Potential

It has been outlined in the previous discussions that the saturation time is dictated by the area that is available on the electrodes for the asphalt droplets to deposit after breaking from the emulsion. Smaller surface area of the cathode implies that less binder is required to saturate the electrode, in other words, less of the emulsion sample is broken in the process. Therefore, reducing the surface area of the cathode in a cationic emulsion will reduce the saturation time. In addition, the total charge flow until saturation also reduces

with the surface area of the cathode (for a cationic emulsion). Figure 4.12 clearly illustrates these results. The repeatability of the results improved with reduced surface area.

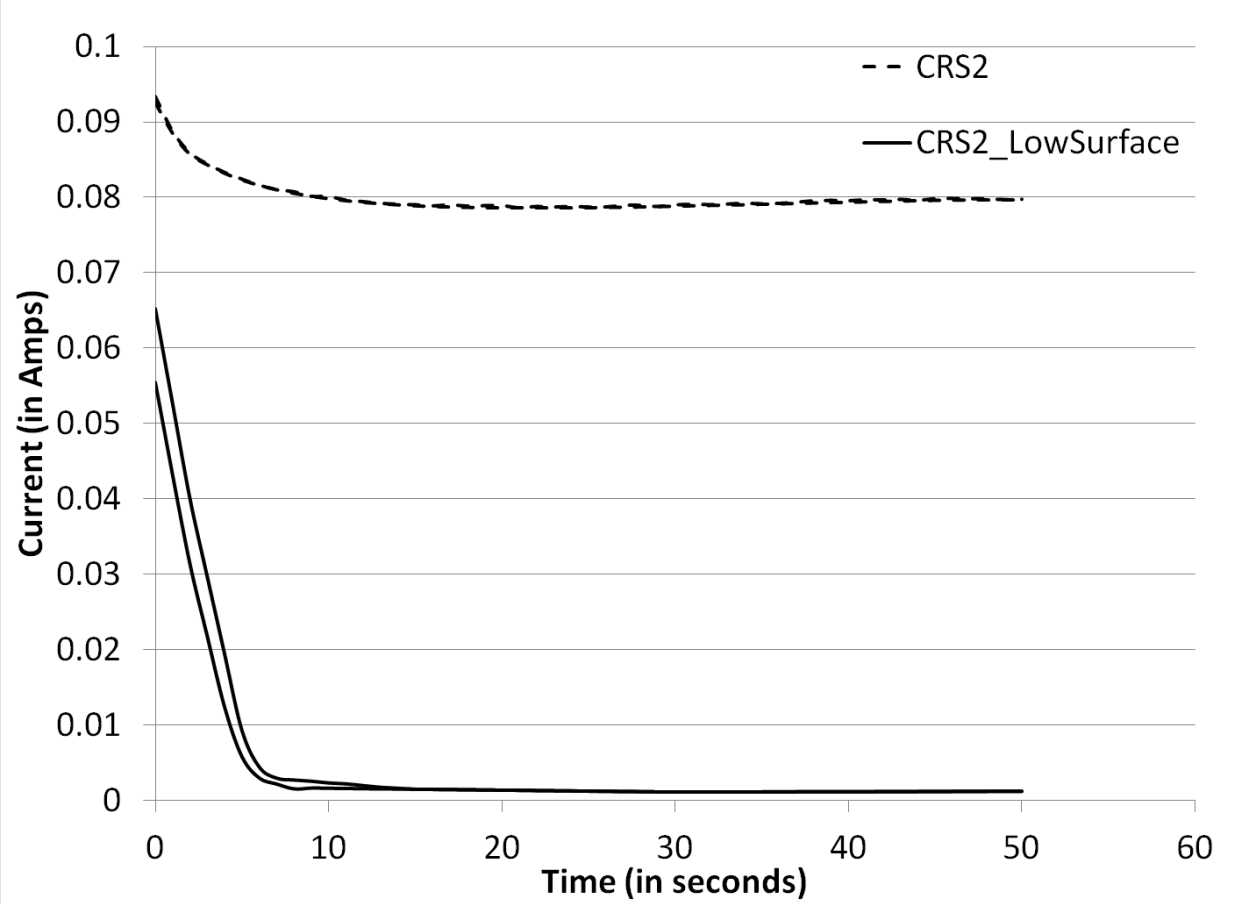


Figure 4.12: Net current flowing through the apparatus with an applied voltage of 18.6V and reduced surface area of the cathode

The current flowing through the apparatus is a function of the strength of the electric field as it governs the electric force acting on the ions and colloid particles alike. Therefore, a reduction in the electric field strength will result in a proportionate reduction in the mobility of the ions and colloid particles. Equation 4.10 suggests that there is

direct relationship between the current flowing through the apparatus and the electric field strength. To verify this assumption, the electric field strength was varied at two levels to determine the sensitivity of the current measurement to the field strength. The results presented in Figure 4.13 suggest that there is a direct relationship between the current flowing through the apparatus and the strength of the electric field. An important observation from these results was that, although the saturation time doubled when the potential was halved, the total charge flow until saturation was the same. This is consistent with the expectation that the total energy required to saturate the electrode should not change significantly with the potential.

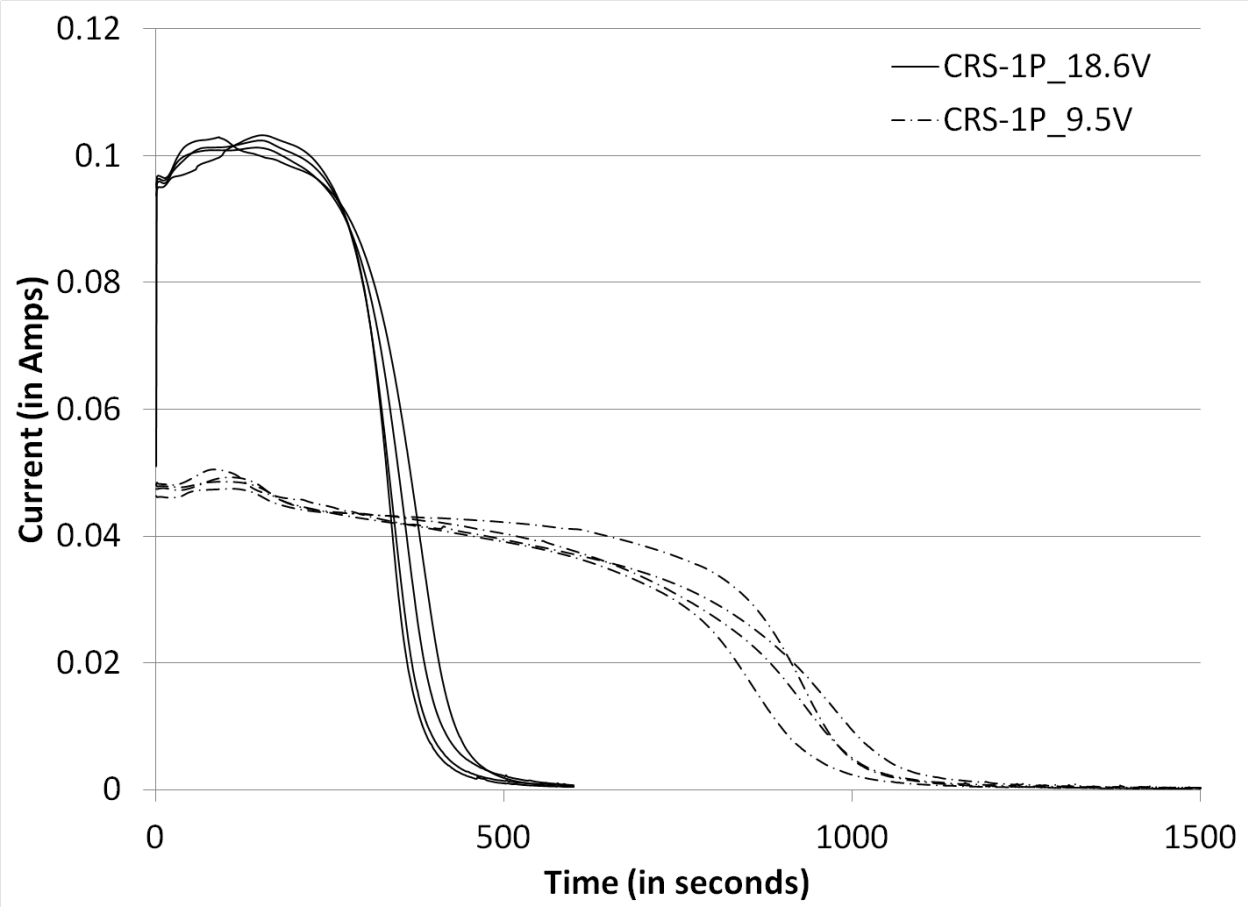


Figure 4.13: Net current flowing through the apparatus with applied voltages of 18.6V and 9.5V for a CRS-1P emulsion sample

Chapter 5: Conclusions and Future Work

5.1. CONCLUSIONS

The goal of this dissertation research was to address a number of issues pertaining to the use and application of surface treatments using asphalt emulsions. The foregoing chapters in this dissertation presented in detail the issues and how these issues can be addressed using a scientific and rational approach as opposed to the experience-based approach which is prevailing nowadays. The following were the major findings from this study.

5.1.1. Curing Trends and Determination of the Time Interval for Placement of Aggregates

- A methodology for the determination of the waiting period before the aggregates can be placed in a chip seal construction job was proposed. The procedure used an empirical approach to equation the rate of moisture loss from the emulsion which is tied to the time to place the aggregates in a chip seal construction job.
- The methodology breaks down the problem into two parts. The first part accounts for the amount of water lost while the emulsion cools down while the second part captures the amount of water lost to evaporation due to the vapor pressure deficit in the ambient air.
- The amount of water lost while the emulsion cools down was modeled as a time dependent variable that is a function of the amount of water present in the system and a temperature specific evaporation coefficient for any given emulsion. The evaporation coefficient is a relative index of the emulsion's response to thermal stimulus in terms of rate of moisture loss, while the time dependent parameter

captures the evolutionary trend of the rate of moisture loss from the system. However, for the conditions tested, results showed that the evaporation coefficient is only dependent on the nature of the emulsion and not the temperature of the system. This was attributed to the skinning effect at the interface. Results indicated that the rate of moisture loss reduces with the square of the residual water in the emulsion.

- Moisture loss can partially be attributed to the vapor pressure deficit in the ambient air. A model based on Meyer's equation was developed to predict the amount of water loss under ambient conditions due to weather conditions, namely: temperature, relative humidity and wind speed.
- In the following step, thresholds were determined on the optimal timing of aggregates at the actual construction site based on the amount of water lost until the aggregates are placed. Field data on the rate of cooling of emulsions were collected along with ambient air temperature, relative humidity and wind speed. Under the assumption that the time to put down the aggregates in each of these field projects provided optimal conditions, the amount of water lost in that time interval was calculated and proposed as the threshold for placing the aggregates.
- The proposed model can be particularly useful to practitioners and field personnel to estimate the time duration between the application of the emulsified binder and the aggregates. It has often been observed that early failures associated with chip seals are largely due to poor adhesion between the binder and the aggregates. To ensure the correct timing of application of aggregates, it is essential to know the

curing characteristics of the emulsified binder because the rate of development of adhesive forces is dependent upon the curing properties of the emulsion. The suggested model will help the field personnel to determine the curing stage of the emulsion at any point in time from the instant it is applied. This will facilitate well-informed decisions on the timing of the aggregate placement.

5.1.2. Setting Rates and Determination of the Optimal Time to Open a Newly Constructed Chip Seal to Traffic

- The second major finding of this dissertation research relates to the rate of setting and the gain in stiffness of a newly constructed chip seal under ambient conditions in the field. The objective of the research was to determine the minimum time to open a newly constructed chip seal to traffic moving at highway speed such that the thin film of asphalt residue left from partial curing of the emulsion offers sufficient resistance to raveling so as to minimize early loss of aggregates.
- The research work focused on data generated from controlled experiments conducted in the laboratory to simulate the most typical materials used for chip seals under typical field conditions in Texas. Based on the analysis of the laboratory data, empirical models were proposed that can predict the amount of water lost due to evaporation as well as the evolution of the rheological properties of the emulsion residue.
- Field evaluations of the setting rate of emulsions were conducted under ambient conditions to obtain critical information in terms of the rate of setting for different

types of emulsions. As part of these field monitoring programs, the rate of setting and the time to open a particular project to traffic was noted – thus helping in determination of the exact time in the evaporation curve when the road was opened to normal traffic (i.e. without any posted speed regulation). The amount of water lost to evaporation in that time interval was defined as the threshold for the predictive model that estimates the setting of emulsion as a function of material properties, weather conditions and time. The amount of water loss as observed in the field monitoring program was correlated with laboratory results to determine the minimum required stiffness for opening a newly constructed chip seal to traffic.

- Results suggest that a stiffness of 2.2 kPa and 4.3 kPa for the residue obtained from partial curing of an anionic and cationic emulsion, respectively, can be considered as the limiting value for satisfactory resistance to raveling for newly constructed chip seals. Based on these thresholds, a methodology to determine the optimal time to open a newly constructed chip seal to highway traffic was proposed, one that ensures satisfactory performance while maximizing operational efficiency.

5.1.3. Developing a Constitutive Equation to Study the Breaking of Emulsions in Electric Fields

- The third finding of this study relates to developing an understanding of the fundamental principles associated with breaking of emulsions when subjected to an electric field and its applications for determining basic emulsion

characteristics. The resulting current flowing through the apparatus represents the material's signature when placed in an electric field. The current flowing through the circuit results from movement of the ionic species in the solution that migrates towards the oppositely charged polarity. The dissolved ions act as carriers of electrical charge and contribute to the flow of current. Key material properties including the zeta potential, viscosity, charge density, and the resistivity of the material were determined.

- The proposed formulation uses Henry's law to associate the flow of current with the mobility of the dissolved ions. The author included two different asphalt emulsions for the validation of the proposed formulation. The current flowing through the material was obtained in real time for each of the emulsion samples as they started to break down in the presence of an electric field, thus providing the validation dataset. The theoretical value of the current was also calculated simultaneously using the proposed formulation (see Equation 4.10). Furthermore, the author also investigated the effect of dilution ratios while cross-validating the proposed equation. It was observed that the current flowing through the apparatus calculated using the proposed equation provided satisfactory resemblance when compared against the validation dataset. However, in the case of the CRS-2P emulsion, the author noticed a difference between the two datasets in the current-time signature at initial stages of the experiment. Nevertheless, the time to reach the asymptotic value was in good agreement in each of the individual experiments. This is particularly important as it provides an insight into the

relative stability of the emulsion as it relates to the energy consumed in breaking of the emulsion. Furthermore it was also observed that the initial current calculated for each of the different samples was in agreement with the measured values. The initial current values, both calculated and measured, followed the same trend, that is, a gradual decrease with increasing dilution ratio. Overall, the proposed formulation provides a valuable insight into the underlying dynamics associated with breaking of asphalt emulsions and a theoretical understanding of the associated fundamental principles.

5.1.4. Developing a Test Methodology for Assessment of Breaking Characteristics of the Emulsion using Electrokinetic Theory

- The final section of this dissertation proposes a test procedure that was developed on the theory presented above to distinguish between different emulsions or changes within a given type of emulsion compared to a reference sample. In the proposed test method an electric potential is applied across an emulsion sample that serves as an electrolytic medium. The current flowing through this setup destabilizes the emulsion and causes the asphalt droplets to break and deposit on one of the electrodes reducing the electric potential experienced by the partially broken emulsion. The test is designed such that this process stops when the amount of asphalt binder deposited on the electrode is adequate to insulate it. The most important feature of this test method is that the current flowing through the set up during the breaking process is recorded in real time. The test method was used with different types of emulsions and also with emulsions that were modified

in the laboratory by further dilution or mechanical agitation. The major findings from this part of the study were as follows.

- The proposed methodology and concomitant variables (saturation time and the total charge flow until saturation) are sensitive to the inherent properties of the emulsion, such as, its dielectric constant, zeta potential and viscosity.
- The two test variables – saturation time and the total charge flow until saturation – provided results that were repeatable for the given material and the test configuration.
- The test variables for the proposed methodology were sensitive to the type of emulsion and relative stability of the emulsion. For example, results indicated that the CRS-2P sample used in this study was relatively more stable than the other two emulsions.
- Test results demonstrate the ability of the proposed method to differentiate between formulations of the same emulsions at different dilution rates with respect to the reference sample.
- The proposed method is sensitive to detect the effect of mechanical agitation on breaking of asphalt emulsions. Results show that there is a significant shift in the current versus time measurements for partially broken emulsions due to mechanical agitation.

The aforementioned conclusions provide evidence suggesting that the test method can be particularly useful as an easy to use quantitative tool to characterize asphalt emulsions and their relative stability. The test method is sensitive to the type of emulsion and

changes within a given type of emulsion. The simplicity of the test set up and repeatability of the results make it particularly useful as an alternative to conventional testing procedures that can be used characterize emulsions in a laboratory or field setup.

5.2. FUTURE WORK

The research work presented in this dissertation addresses several research needs associated with chip seal construction practices and the use of asphalt emulsions. However, the author foresees a few aspects of this study that needs further investigation. Firstly, the thresholds proposed for the shear stiffness and the setting of surface treatments is based on a limited number of data points. The author considers that a well-designed experimental design with at least 10 separate field trials and sampling projects from different geographical regions can improve the confidence in the proposed cutoff values.

Secondly, the theoretical formulation of the current flowing through the circuit accounted for changes in viscosity, ionic concentration and the voltage drop across the circuit due to deposition of the asphalt particles on the electrodes. However, the secondary electrochemical reactions occurring in the apparatus alter the pH of solution which will affect the ζ-potential of the emulsion and ultimately alter the mobility of the dissolved ions. Under the scope of this study, this particular fact has been ignored and the effect of ζ-potential on the mobility values is not accounted for. It is, therefore, recommended that the effect of zeta potential on the mobility is investigated and the proposed model is revised while taking this factor into account.

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